CHAPTER 5
THERMOCHEMISTRY

5.1 ENERGY

ENERGY

> **Energy** is the ability to do work or transfer heat.

Energy used to cause an object that has mass to move is called **work.**

- Energy used to cause the temperature of an object to rise is called **heat.**
- This chapter is about **thermodynamics,** which is the study of energy transformations, and **thermochemistry,** which applies the field to chemical reactions, specifically.

Why is a pitcher able to throw a baseball faster than he could throw a bowling ball?

a. It is harder to hold a baseball than a bowling ball.

b. For the same input of energy, an object of smaller mass will have the larger speed.

c. For the same input of energy, an object of larger mass will have the larger speed.

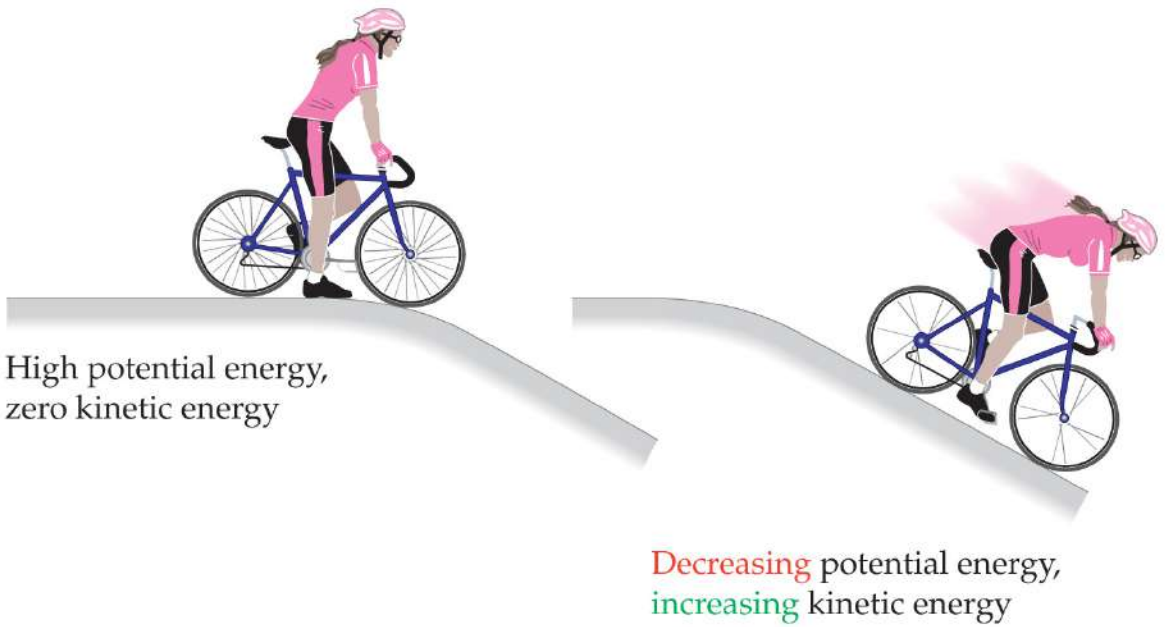
d. The spinning of the bowling ball causes it to drop to the ground faster.

(a)

KINETIC ENERGY

Kinetic energy is energy an object possesses by virtue of its motion:

$$E_k = \frac{1}{2}mv^2$$



Suppose the bicyclist is coasting (not pedaling) at constant speed on a flat road and begins to go up a hill. If she does not start pedaling, what happens to her speed? Why?

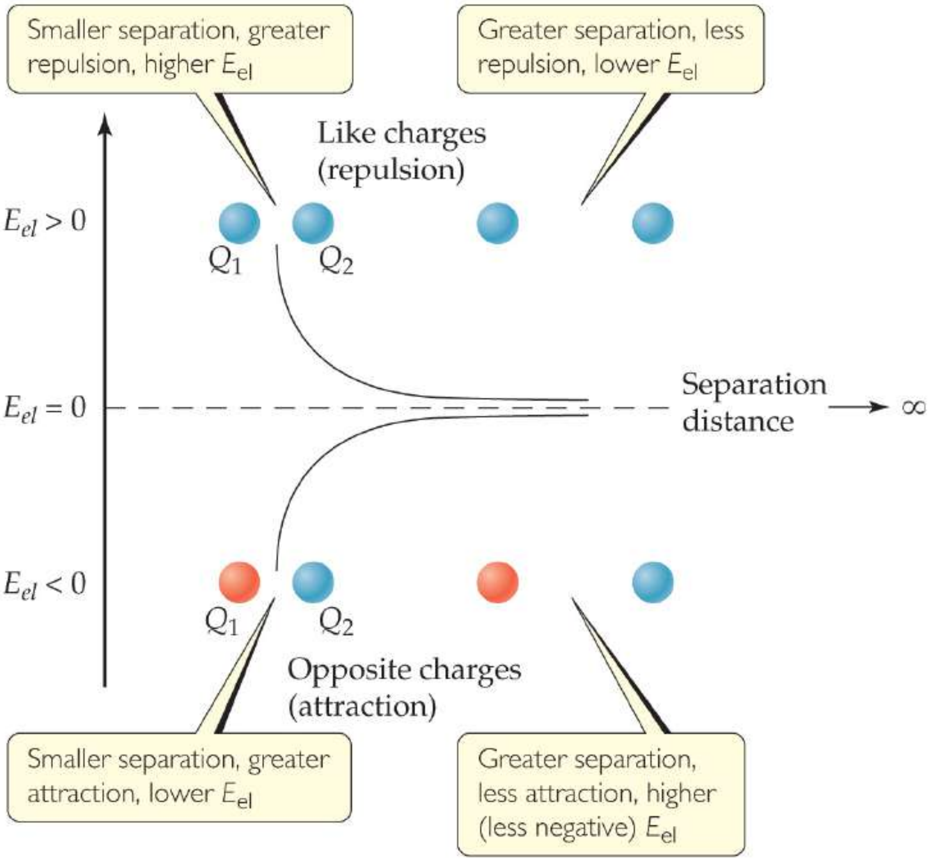
a. Increases as potential energy is converted to kinetic energy

b. Increases as the kinetic energy is converted to potential energy

c. Decreases as potential energy is converted to kinetic energy

d. Decreases as the kinetic energy is converted to potential energy

POTENTIAL ENERGY



Potential energy is energy an object possesses by virtue of its position or chemical composition.

The most important form of potential energy in molecules is electrostatic potential energy, E_{el}:

$$E_{el} = \frac{\kappa Q_1 Q_2}{d}$$

A positively charged particle and a negatively charged particle are initially far apart. What happens to their electrostatic potential energy as they are brought closer together?

a. Becomes more positive and decreasing in absolute magnitude

b. Becomes more negative and increasing in absolute magnitude

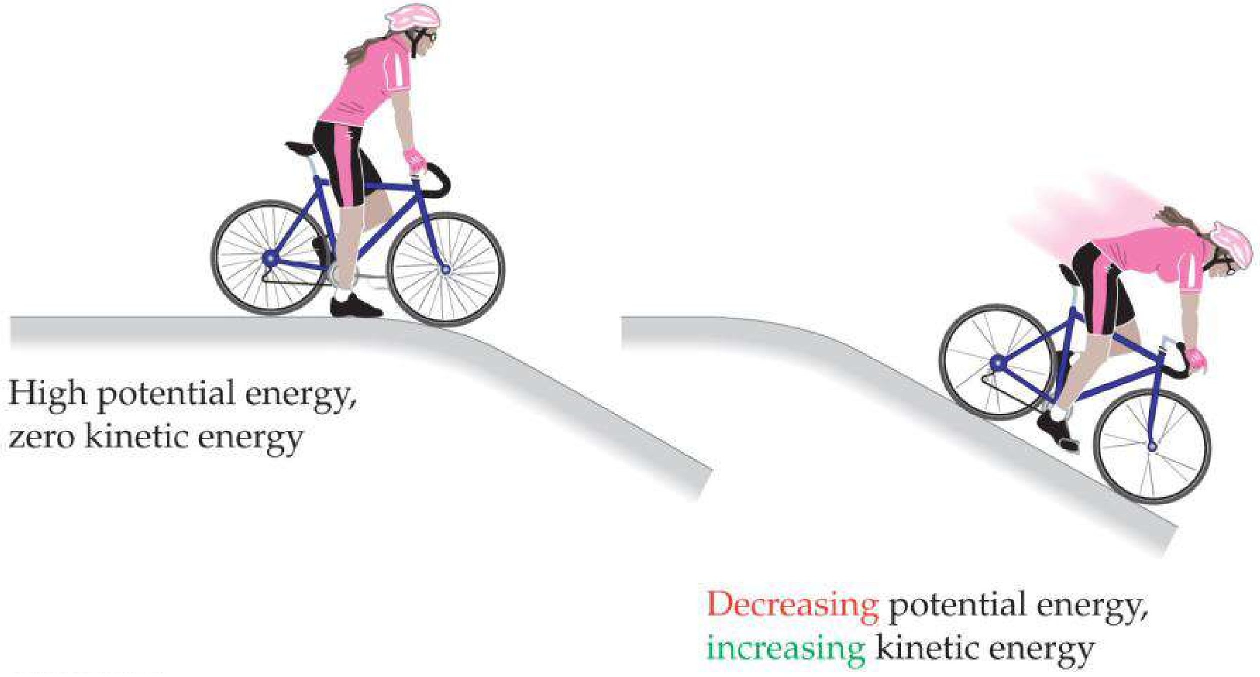
c. Becomes more positive and increasing in absolute magnitude

d. Becomes more negative and decreasing in absolute magnitude

The cyclist and bicycle come to a stop at the bottom of the hill.

Is the potential energy the same as it was at the top of the hill?

a. Yes
b. No

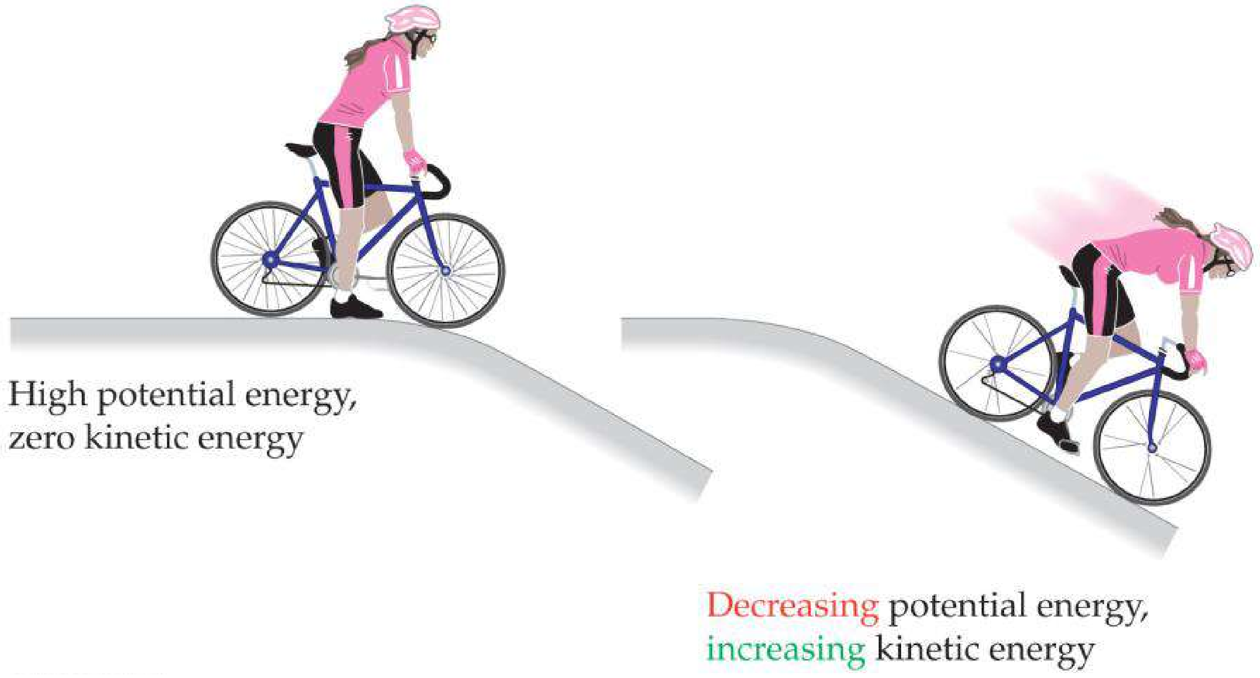


The cyclist and bicycle come to a stop at the bottom of the hill.

Is the kinetic the same as it was at the top of the hill?

a. Yes

b. No



UNITS OF ENERGY

The SI unit of energy is the **joule (*J*)**:

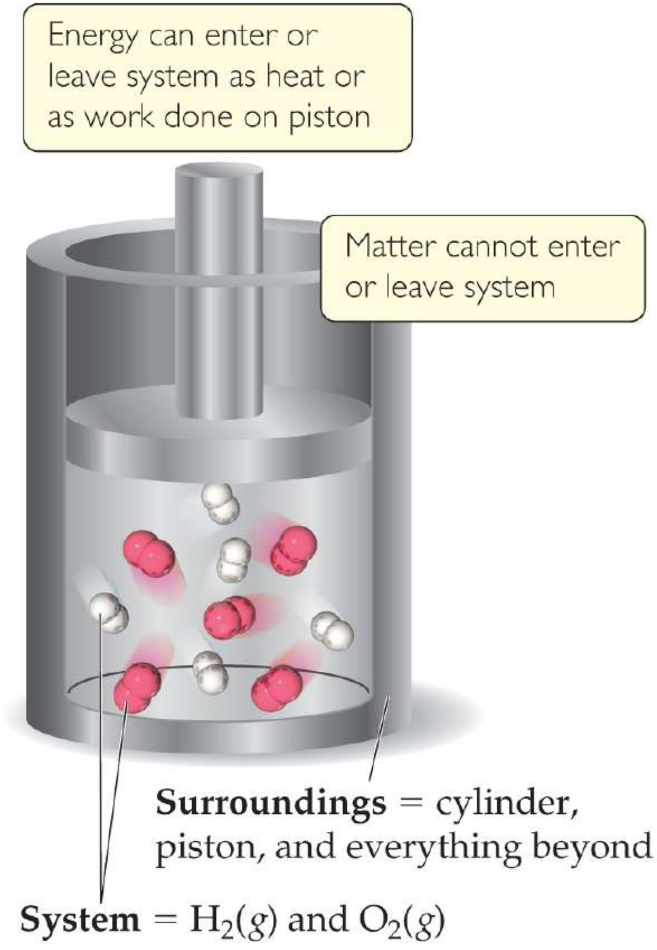
$$1\ \mathrm{J} = 1\ \frac{\mathrm{kg\ m^2}}{\mathrm{s^2}}$$

An older, non-SI unit is still in widespread use, the **calorie (*cal*)**:

$$1\ \mathrm{cal} = 4.184\ \mathrm{J}$$

(Note: this is *not* the same as the calorie of foods; the food calorie is 1 kcal!)

DEFINITIONS: SYSTEM AND SURROUNDINGS



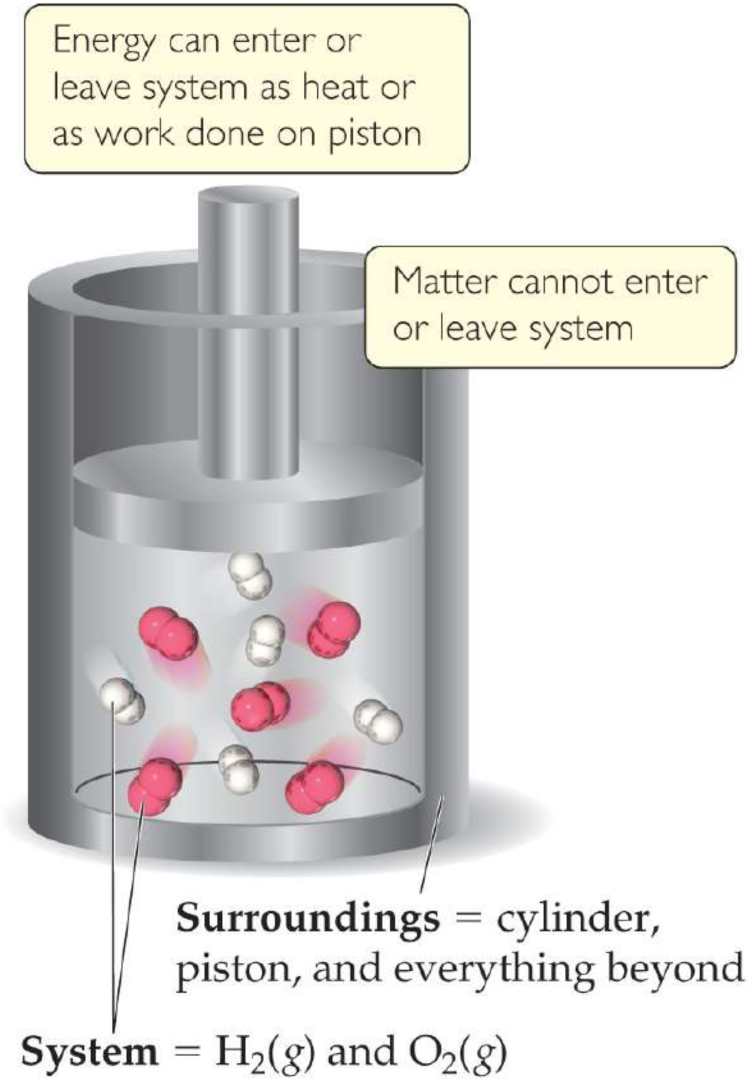
The **system** includes the molecules we want to study (here, the hydrogen and oxygen molecules).

The **surroundings** are everything else (here, the cylinder and piston).

If the piston is pulled upward so that it sits halfway between the position shown and the top of the cylinder, is the system still closed?

a. Yes, because matter is not transferred to the surroundings.

b. No, because matter is transferred to the surroundings.



Is a human being an isolated, closed, or open system?

a. Closed system
b. Isolated system
c. Open system

DEFINITIONS: WORK

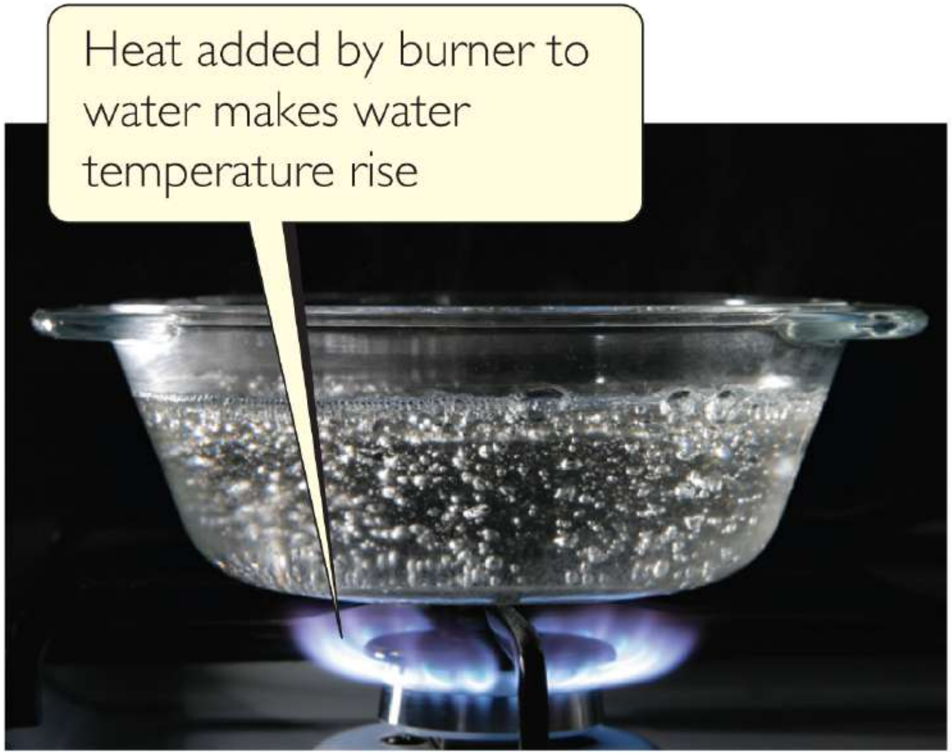
Energy used to move an object over some distance is **work:**

$w = F \times d$

where *w* is work, *F* is the force, and *d* is the distance over which the force is exerted.

Work done by pitcher on ball to make ball move

HEAT


Heat added by burner to water makes water temperature rise

Energy can also be transferred as heat.

Heat flows from warmer objects to cooler objects.

DESCRIBING AND CALCULATING ENERGY CHANGES: SAMPLE EXERCISE 5.1

A bowler lifts a 5.4 kg (12-lb) bowling ball from ground level to a height of 1.6 m and then drops the ball back to the ground.

- A) What happens to the potential energy of the ball as it is raised?
- B) How much work is used to raise the ball?
- C) If all of the work in (B) is converted to kinetic energy, what is the speed of the ball just before it hits the ground?

Practice Exercise 1

Which of the following objects has the greatest kinetic energy?

(**a**) a 500-kg motorcycle moving at 100 km/h

(**b**) a 1,000-kg car moving at 50 km/h

(**c**) a 1,500-kg car moving at 30 km/h

(**d**) a 5,000-kg truck moving at 10 km/h

(**e**) a 10,000-kg truck moving at 5 km/h

PRACTICE EXERCISE 2

What is the kinetic energy of:

- A) an Ar atom moving with a speed of 650 m/s
- B) a mole of Ar atoms moving with a speed of 650 m/s (1 amu = 1.66 x 10^{-27} kg)

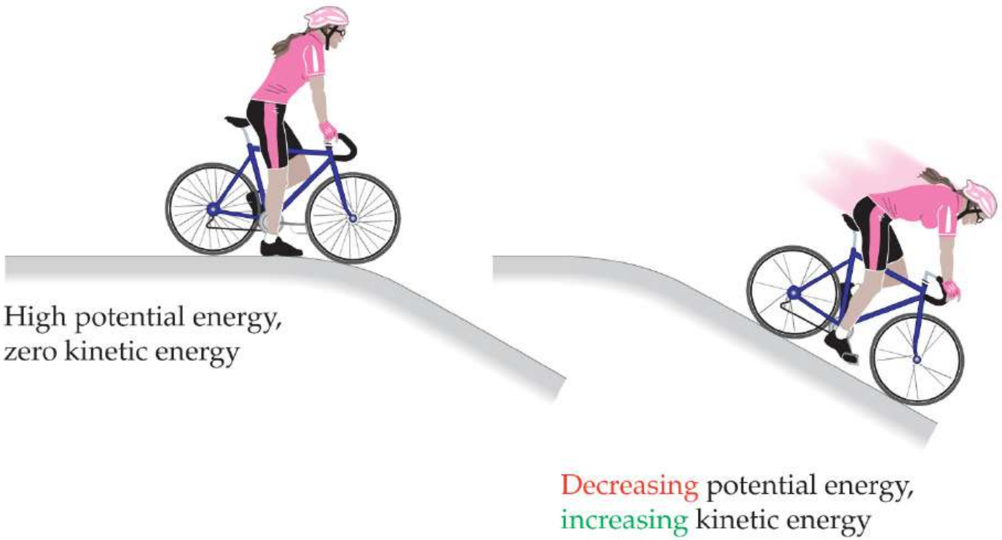
5.2 THE FIRST LAW OF THERMODYNAMICS

CONVERSION OF ENERGY

Energy can be converted from one type to another.

The cyclist has potential energy as she sits on top of the hill.

As she coasts down the hill, her potential energy is converted to kinetic energy until the bottom, where the energy is converted to kinetic energy.



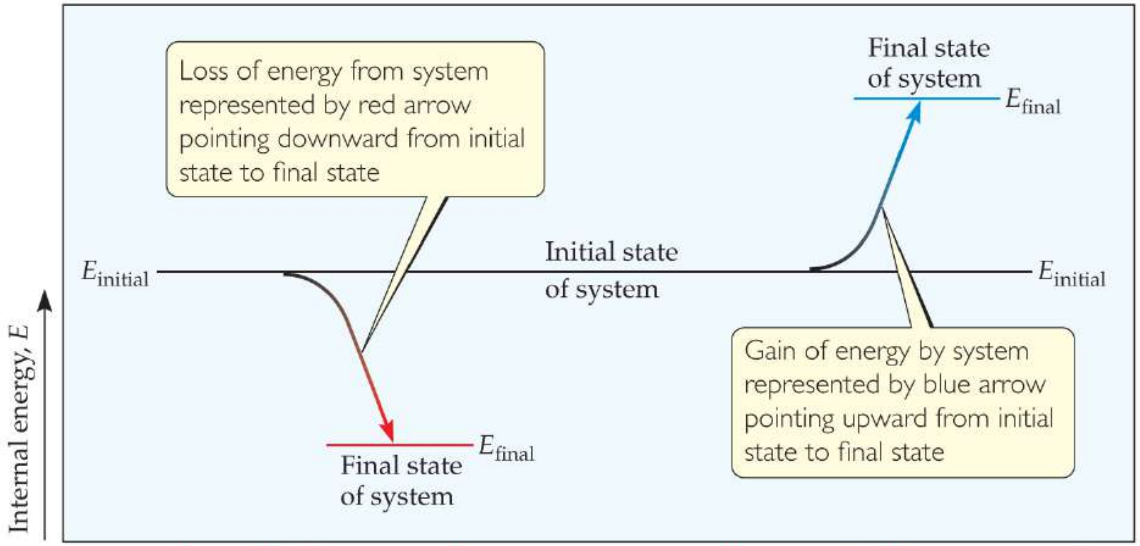
FIRST LAW OF THERMODYNAMICS

Energy is neither created nor destroyed.

In other words, the total energy of the universe is a constant; if the system loses energy, it must be gained by the surroundings, and vice versa.

INTERNAL ENERGY

The **internal energy** of a system is the sum of all kinetic and potential energies of all components of the system; we call it *E*.



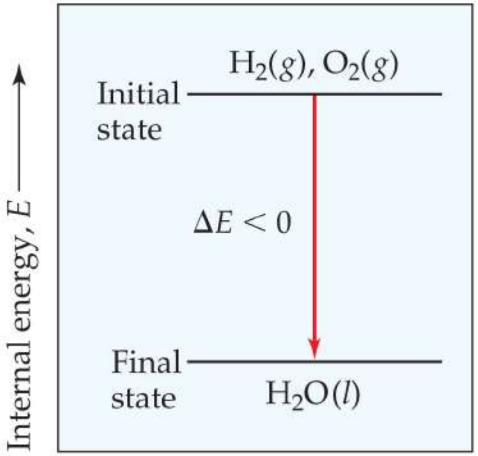
Energy lost to surroundings, internal energy of system decreases, ΔE negative

Energy gained from surroundings, internal energy of system increases, ΔE positive

INTERNAL ENERGY

By definition, the change in internal energy, ΔE, is the final energy of the system minus the initial energy of the system:

$$\Delta E = E_{\text{final}} - E_{\text{initial}}$$

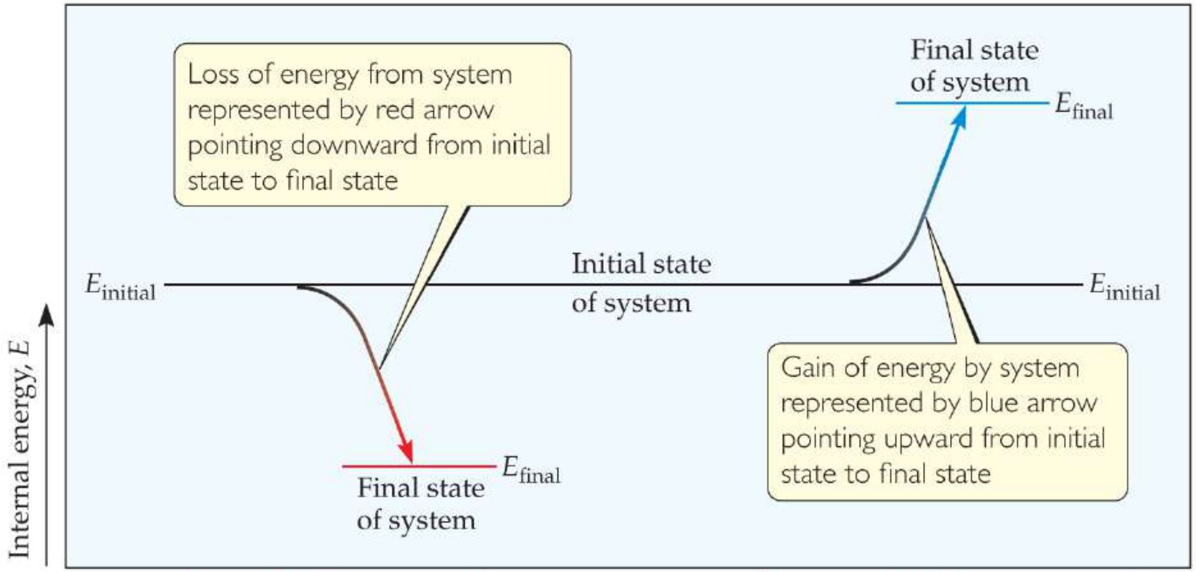


E_{initial} greater than E_{final}; therefore, energy is released from system to surroundings during reaction and $\Delta E < 0$

CHANGES IN INTERNAL ENERGY

If $\Delta E > 0$, $E_{\text{final}} > E_{\text{initial}}$

- Therefore, the system *absorbed* energy from the surroundings.
- This energy change is called **endergonic.**



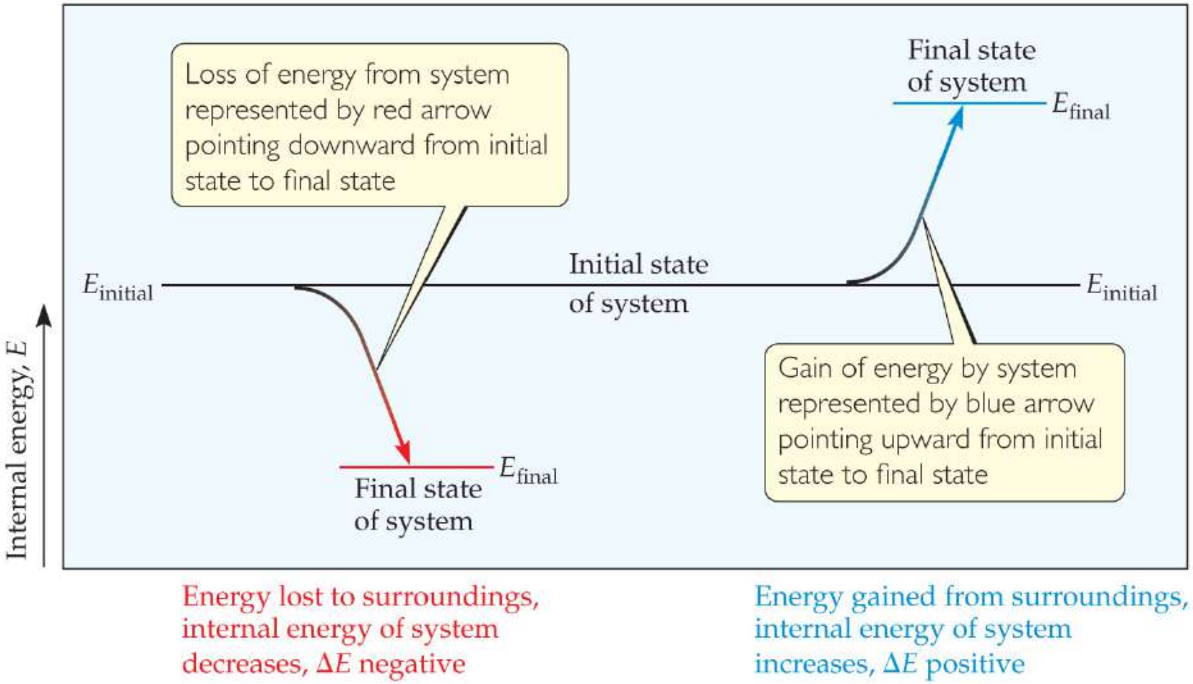
Energy lost to surroundings, internal energy of system decreases, ΔE negative

Energy gained from surroundings, internal energy of system increases, ΔE positive

CHANGES IN INTERNAL ENERGY

If $\Delta E < 0$, $E_{\text{final}} < E_{\text{initial}}$

- Therefore, the system *released* energy to the surroundings.
- This energy change is called **exergonic**



Energy lost to surroundings, internal energy of system decreases, ΔE negative

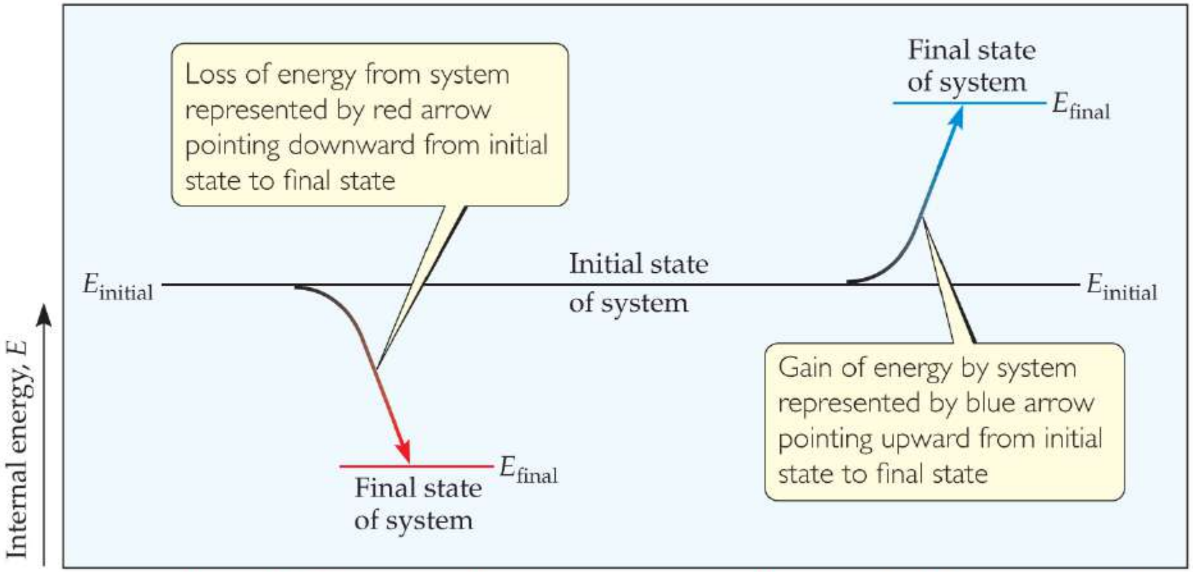
Energy gained from surroundings, internal energy of system increases, ΔE positive

What is the value of Δ if E_{final} equals $E_{initial}$?

a. Positive number

b. Zero

c. Negative number

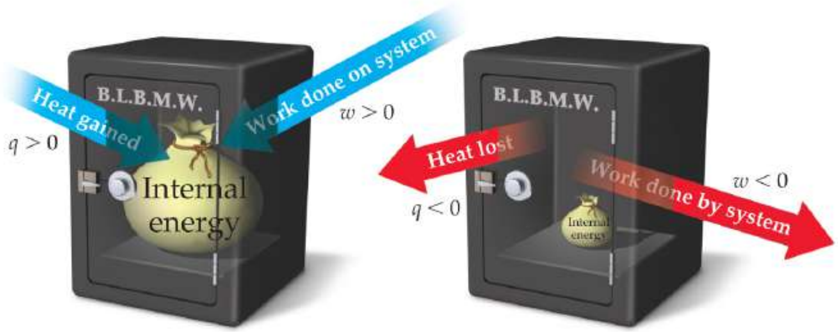


Energy lost to surroundings, internal energy of system decreases, ΔE negative

Energy gained from surroundings, internal energy of system increases, ΔE positive

CHANGES IN INTERNAL ENERGY

System is interior of vault



Energy deposited into system
$\Delta E > 0$

Energy withdrawn from system
$\Delta E < 0$

When energy is exchanged between the system and the surroundings, it is exchanged as either heat (*q*) or work (*w*).

That is, $\Delta E = q + w$.

Δ*E*, *Q*, *W*, AND THEIR SIGNS

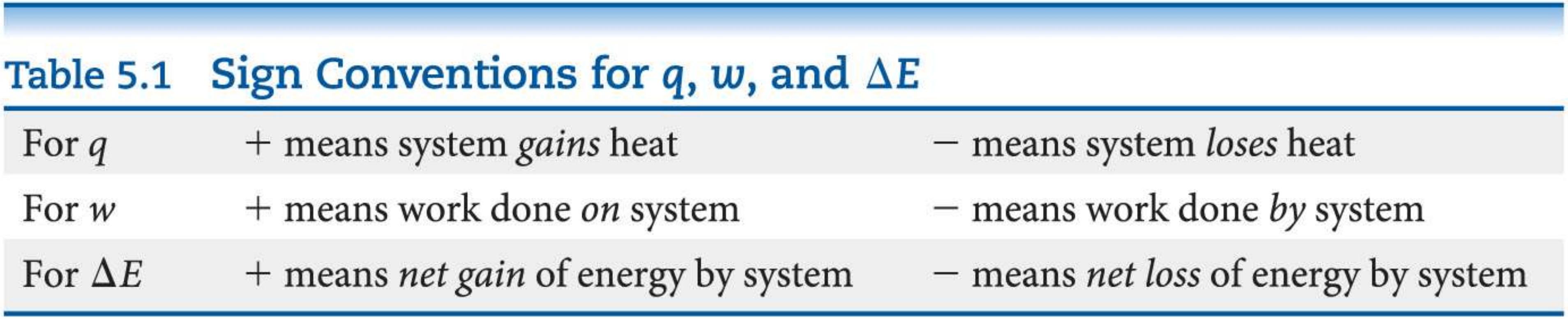


Table 5.1 Sign Conventions for q, w, and ΔE

For q	+ means system *gains* heat	− means system *loses* heat
For w	+ means work done *on* system	− means work done *by* system
For ΔE	+ means *net gain* of energy by system	− means *net loss* of energy by system

SAMPLE EXERCISE 5.2

Two gases, A(*g*) and B(*g*), are confined in a cylinder-and-piston. Substances A and B react to form a solid product:

$A(g) + B(g) \rightarrow C(s)$. As the reaction occurs, the system loses 1150 J of heat to the surroundings. The piston moves downward as the gases react to form a solid. As the volume of the gas decreases under the constant pressure of the atmosphere, the surroundings do 480 J of work on the system. What is the change in the internal energy of the system?

Practice Exercise 1

Consider the following four cases: **(i)** A chemical process in which heat is absorbed, **(ii)** A change in which $q = 30$ J, $w = 44$ J, **(iii)** A process in which a system does work on its surroundings with no change in q, **(iv)** A process in which work is done on a system and an equal amount of heat is withdrawn.

In how many of these cases does the internal energy of the system decrease?

(a) 0
(b) 1
(c) 2
(d) 3

PRACTICE EXERCISE 2

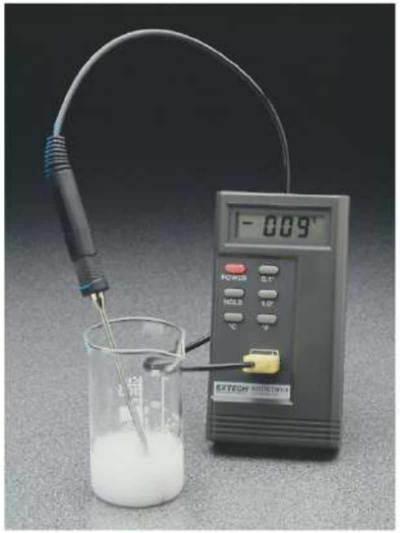
Calculate the change in the internal energy of the system for a process in which the system absorbs 140 J of heat from the surroundings and does 85 J of work on the surroundings.

EXCHANGE OF HEAT BETWEEN SYSTEM AND SURROUNDINGS

When heat is absorbed by the system from the surroundings, the process is **endothermic.**

System: reactants + products

Surroundings: solvent, initially at room temperature



(a) An endothermic reaction

Heat flows from surroundings into system, temperature of surroundings drops, thermometer reads temperature well below room temperature

EXCHANGE OF HEAT BETWEEN SYSTEM AND SURROUNDINGS

When heat is released by the system into the surroundings, the process is **exothermic.**

System: reactants + products

Surroundings:
air around reactants

(b) An exothermic reaction

Heat flows (violently) from system into surroundings, temperature of surroundings increases

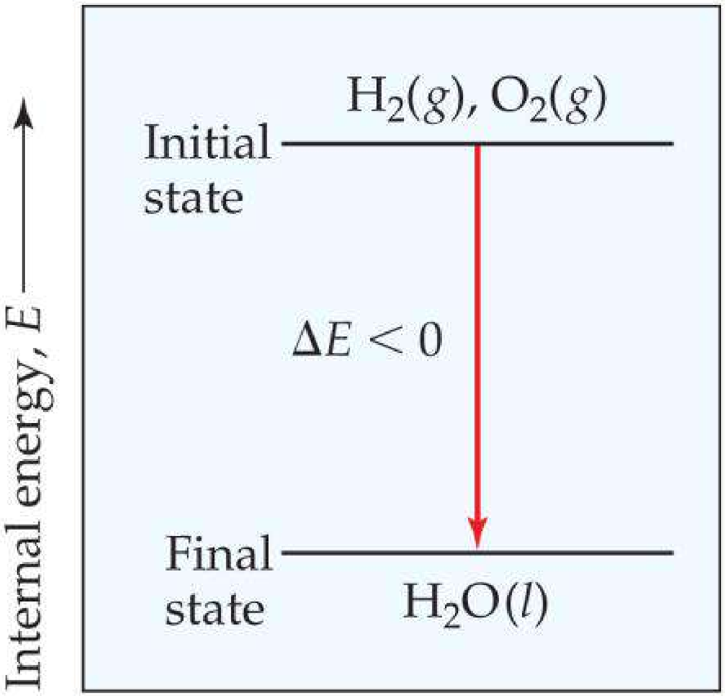
When $H_2(g)$ and $O_2(g)$ react to form $H_2O(l)$, heat is released to the surroundings. Consider the reverse reaction, namely, the formation of $H_2(g)$ and $O_2(g)$ from $H_2O(l)$: $2\ H_2O(l) \longrightarrow 2\ H_2(g) + O_2(g)$. Is this reaction exothermic or endothermic?

a. Endothermic, because heat is released to the surroundings

b. Exothermic, because heat is released to the surroundings

c. Endothermic, because heat is absorbed from the surroundings

d. Exothermic, because heat is absorbed from the surroundings



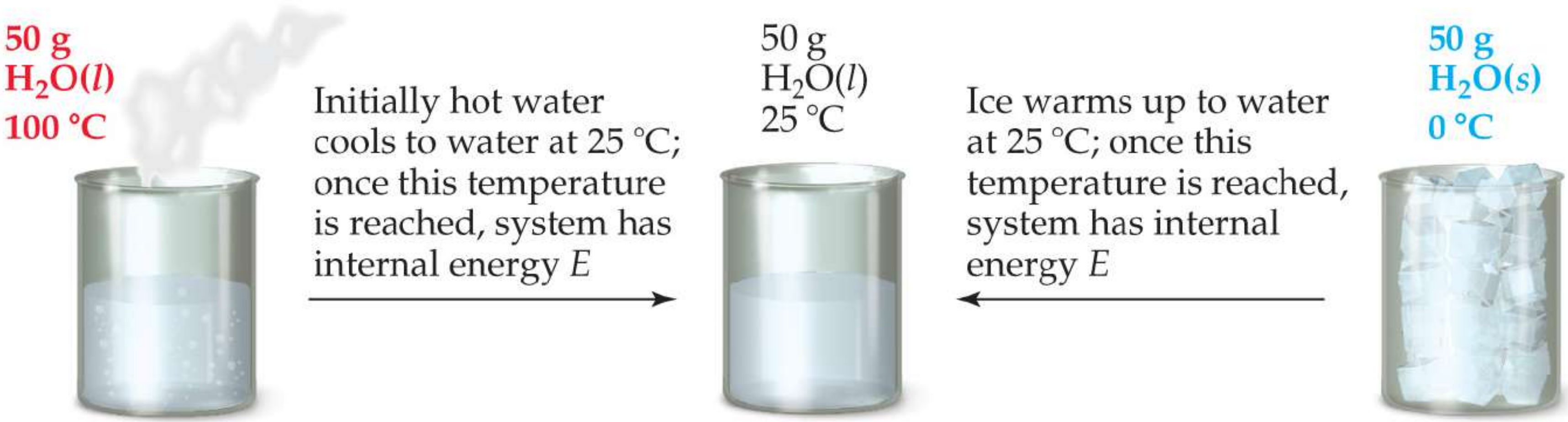
$E_{initial}$ greater than E_{final}; therefore, energy is released from system to surroundings during reaction and $\Delta E < 0$

STATE FUNCTIONS

Usually we have no way of knowing the internal energy of a system; finding that value is simply too complex a problem.

However, we do know that the internal energy of a system is independent of the path by which the system achieved that state.

- In the system below, the water could have reached room temperature from either direction.



Initially hot water cools to water at 25 °C; once this temperature is reached, system has internal energy *E*

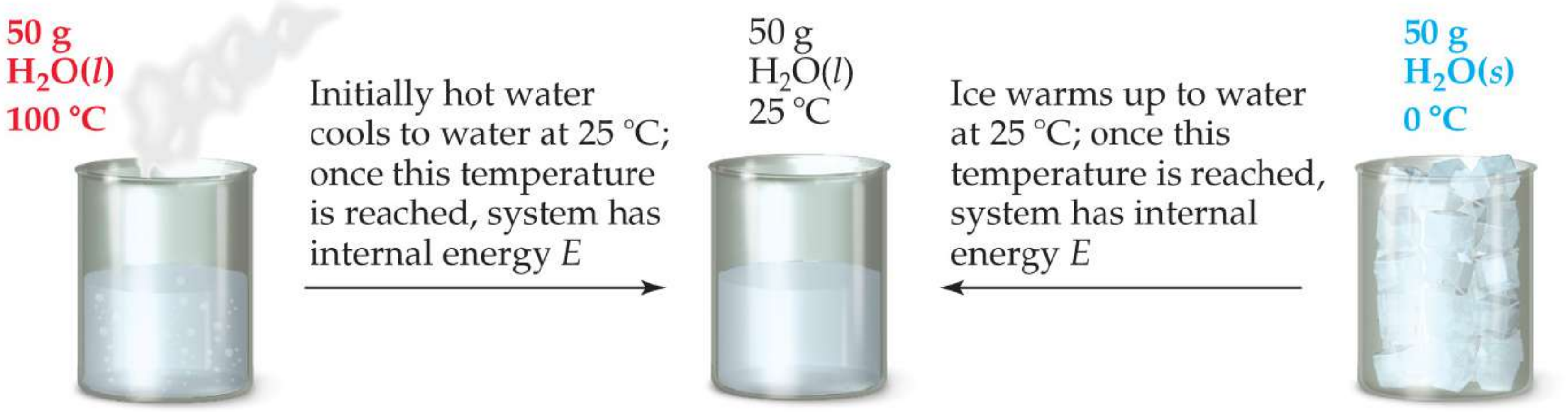
Ice warms up to water at 25 °C; once this temperature is reached, system has internal energy *E*

STATE FUNCTIONS

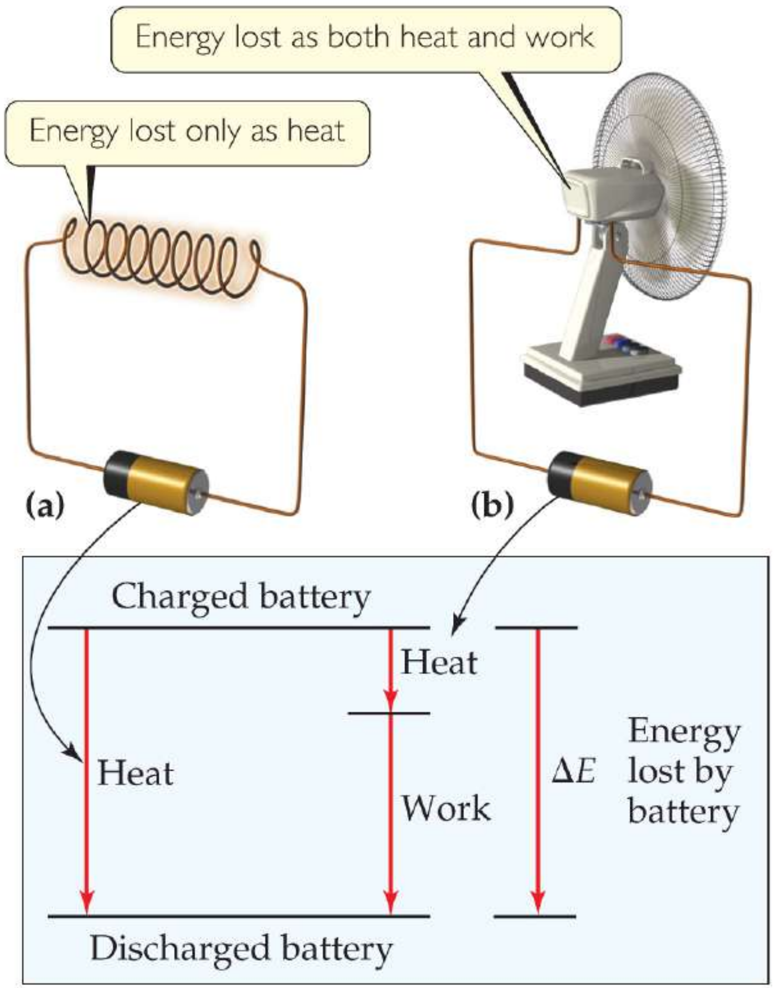
Therefore, internal energy is a state function.

It depends only on the present state of the system, not on the path by which the system arrived at that state.

And so, ΔE depends only on E_{initial} and E_{final}.



STATE FUNCTIONS



However, *q* and *w* are *not* state functions.

Whether the battery is shorted out or is discharged by running the fan, its ΔE is the same.

- But *q* and *w* are different in the two cases.

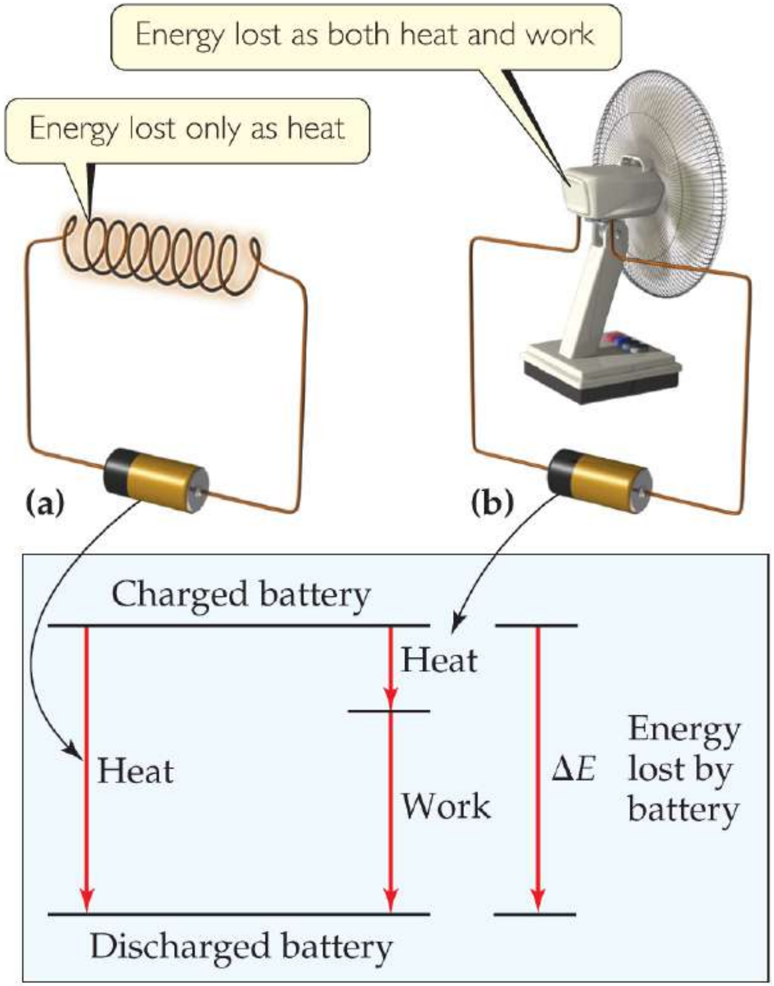
If the battery is defined as the system, what is the sign on *w* in part (b)?

a. $w > 0$

b. $w = 0$

c. $w < 0$

d. Cannot be determined



In what ways is the balance in your checkbook a state function?

a. It is determined by many factors and involves data such as the number of checks, date, and payee.

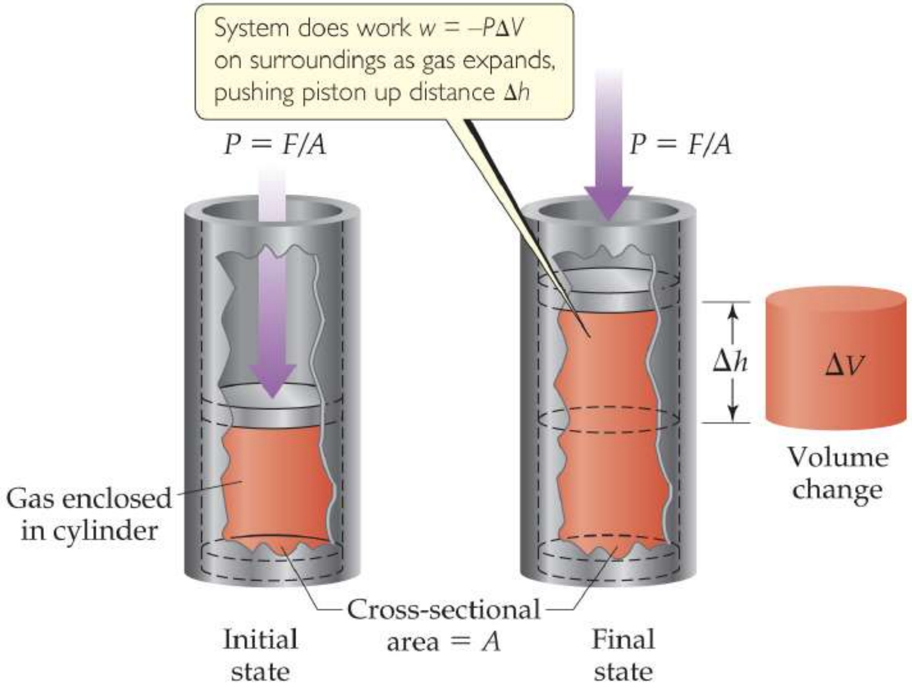
b. It is a numerical value calculated from known amounts of checks.

c. It is calculated from multiple transactions.

d. It only depends on the net total of all transactions, and not on the ways money is transferred into or out of the account.

5.3 ENTHALPY

WORK

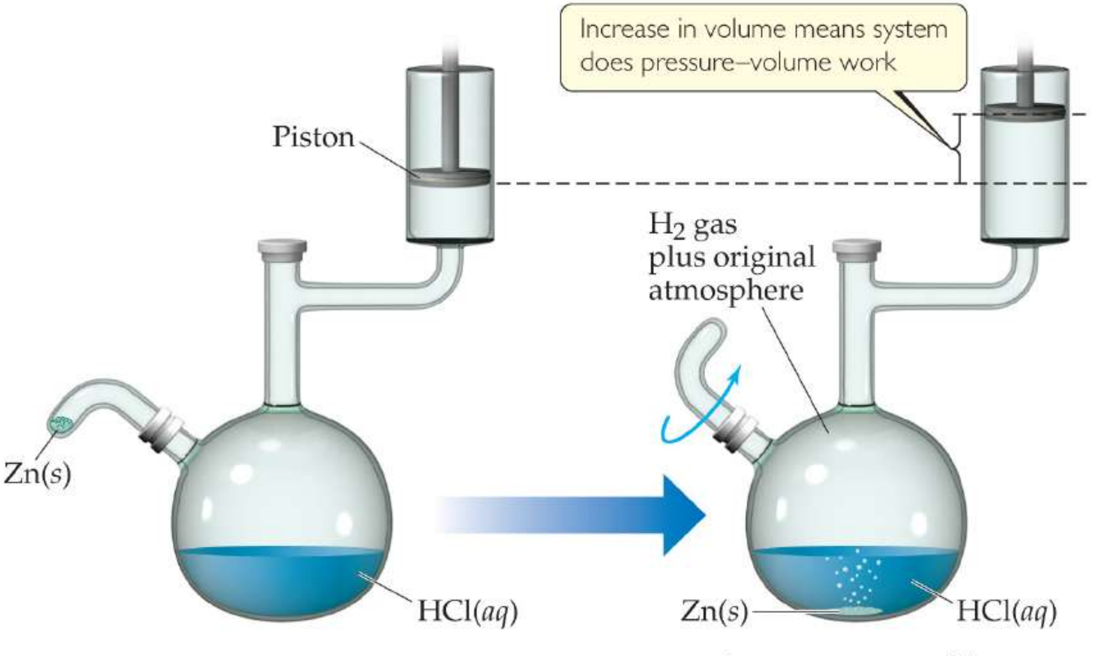


Usually in an open container the only work done is by a gas pushing on the surroundings (or by the surroundings pushing on the gas).

WORK

We can measure the work done by the gas if the reaction is done in a vessel that has been fitted with a piston:

$$w = -P\Lambda V$$



Increase in volume means system does pressure–volume work

$$Zn(s) + 2\,H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$$

If the amount of zinc used in the reaction is increased, will more work be done by the system? Is there additional information you need in order to answer this question?

a. If Zn(*s*) is the limiting reactant, then more gas is formed and more work will be done.

b. If Zn(*s*) is the limiting reactant, then less gas is produced and less work will be done.

c. If HCl(*aq*) is the limiting reactant, then addition of Zn(*s*) increases the amount of gas formed and more work is done.

d. If HCl(*aq*) is the limiting reactant, then addition of Zn(*s*) decreases the amount of gas formed and less work is done.

If a system does not change its volume during the course of a process, does it do pressure–volume work?

a. Yes, because pressure may change the value of work in $w = -P\Delta V$.

b. No, because $\Delta V = 0$.

Sample Exercise 5.3

A fuel is burned in a cylinder equipped with a piston. The initial volume of the cylinder is 0.250 L, and the final volume is 0.980 L. If the piston expands against a constant pressure of 1.35 atm, how much work (in J) is done?
(1 L-atm = 101.3 J)

Practice Exercise 1

If a balloon is expanded from 0.055 to 1.403 L against an external pressure of 1.02 atm, how many L-atm of work is done?

(a) −0.056 L-atm
(b) −1.37 L-atm
(c) 1.43 L-atm
(d) 1.49 L-atm
(e) 139 L-atm

Practice Exercise 2

Calculate the work, in J, if the volume of a system contracts from 1.55 to 0.85 L at a constant pressure of 0.985 atm.

ENTHALPY

If a process takes place at constant pressure (as the majority of processes we study do) and the only work done is this pressure–volume work, we can account for heat flow during the process by measuring the *enthalpy* of the system.

Enthalpy is the internal energy plus the product of pressure and volume:

$$H = E + PV$$

ENTHALPY

When the system changes at constant pressure, the change in enthalpy, ΔH, is

$$\Delta H = \Delta(E + PV)$$

This can be written

$$\Delta H = \Delta E + P\Delta V$$

ENTHALPY

Since $\Delta E = q + w$ and $w = -P\Delta V$, we can substitute these into the enthalpy expression:

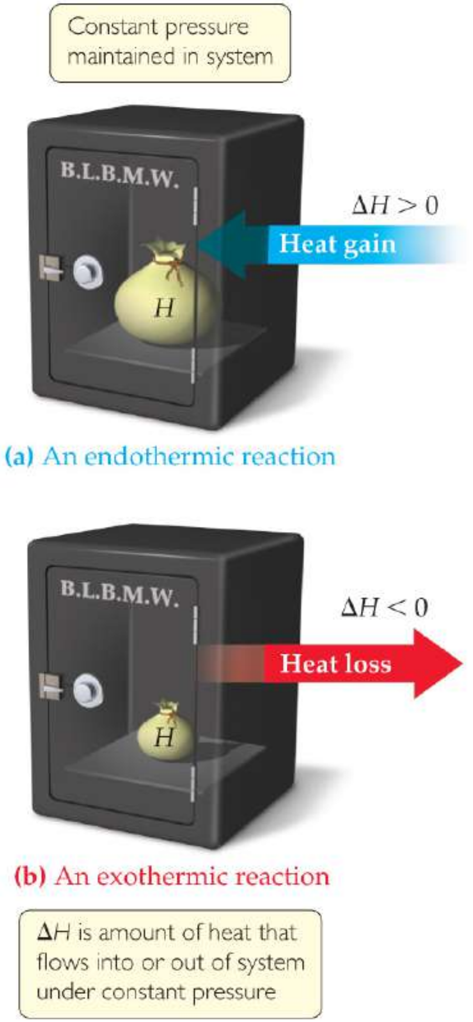
$$\Delta H = \Delta E + P\Delta V$$

$$\Delta H = (q + w) - w$$

$$\Delta H = q$$

So, at constant pressure, the change in enthalpy *is* the heat gained or lost.

ENDOTHERMIC AND EXOTHERMIC



A process is endothermic when ΔH is positive.

A process is exothermic when ΔH is negative.

When a reaction occurs in a flask, you notice that the flask gets colder. What is the sign of ΔH?

a. $+$
b. $-$
c. Neither; $\Delta H = 0$

SAMPLE EXERCISE 5.4

Indicate the sign of the enthalpy change, ΔH, in each of the following processes carried out under atmospheric pressure, and indicate whether the process is endothermic or exothermic: (**a**) An ice cube melts; (**b**) 1 g of butane (C_4H_{10}) is combusted in sufficient oxygen to give complete combustion to CO_2 and H_2O.

Practice Exercise 1

A chemical reaction that gives off heat to its surroundings is said to be _______________ and has a _______________ value of ΔH.

(a) endothermic, positive

(b) endothermic, negative

(c) exothermic, positive

(d) exothermic, negative

Practice Exercise 2

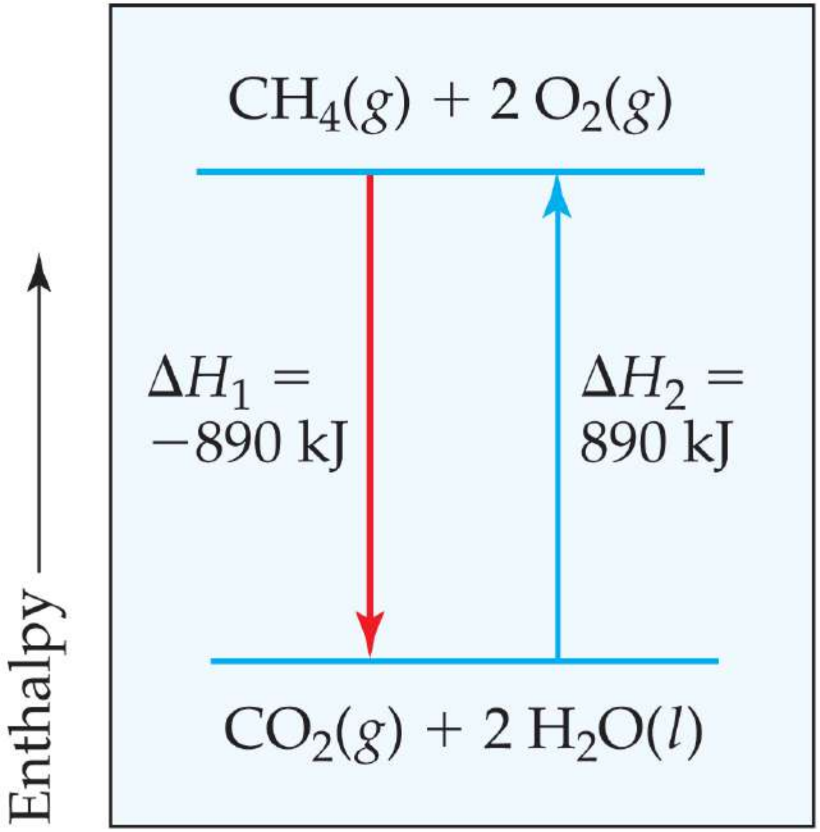
Molten gold poured into a mold solidifies at atmospheric pressure. With the gold defined as the system, is the solidification an exothermic or endothermic process?

5.4 ENTHALPIES OF REACTION

ENTHALPY OF REACTION

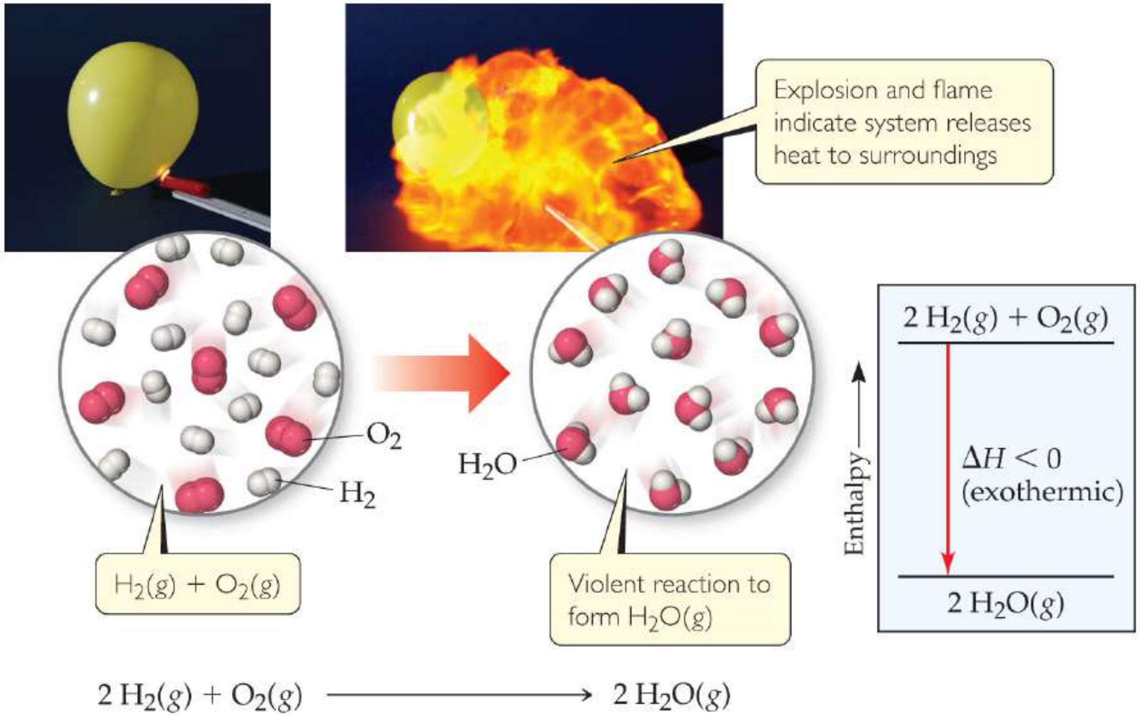
The *change* in enthalpy, ΔH, is the enthalpy of the products minus the enthalpy of the reactants:

$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$



ENTHALPY OF REACTION

This quantity, ΔH, is called the **enthalpy of reaction,** or the **heat of reaction.**



$2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O(g)$

If the reaction to form water were written $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g)$, would you expect the same value of ΔH as in the equation $2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(g)$? Why or why not?

a. Yes, because the reactants and products are the same.

b. No, because only half as much matter is involved.

c. Yes, because mass does not affect enthalpy change.

d. No, because enthalpy is a state function.

THE TRUTH ABOUT ENTHALPY

1. Enthalpy is an extensive property.
2. ΔH for a reaction in the forward direction is equal in size, but opposite in sign, to ΔH for the reverse reaction.
3. ΔH for a reaction depends on the state of the products and the state of the reactants.

SAMPLE EXERCISE 5.5

How much heat is released when 4.50 g of methane gas is burned in a constant pressure system?

$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)}$

$\Delta H = -890\ kJ$

Practice Exercise 1

The complete combustion of ethanol, C_2H_5OH (FW = 46.0 g/mol), proceeds as follows:

$C_2H_5OH(l) + 3 \rightarrow O_2(g)\ 2CO_2(g) + 3H_2O(l) \qquad \Delta H = -555\ \text{kJ}$

What is the enthalpy change for combustion of 15.0 g of ethanol?

(a) −12.1 kJ

(b) −181 kJ

(c) −422 kJ

(d) −555 kJ

(e) −1700 kJ

PRACTICE EXERCISE 2

Hydrogen peroxide can decompose to water and oxygen by the following reaction:

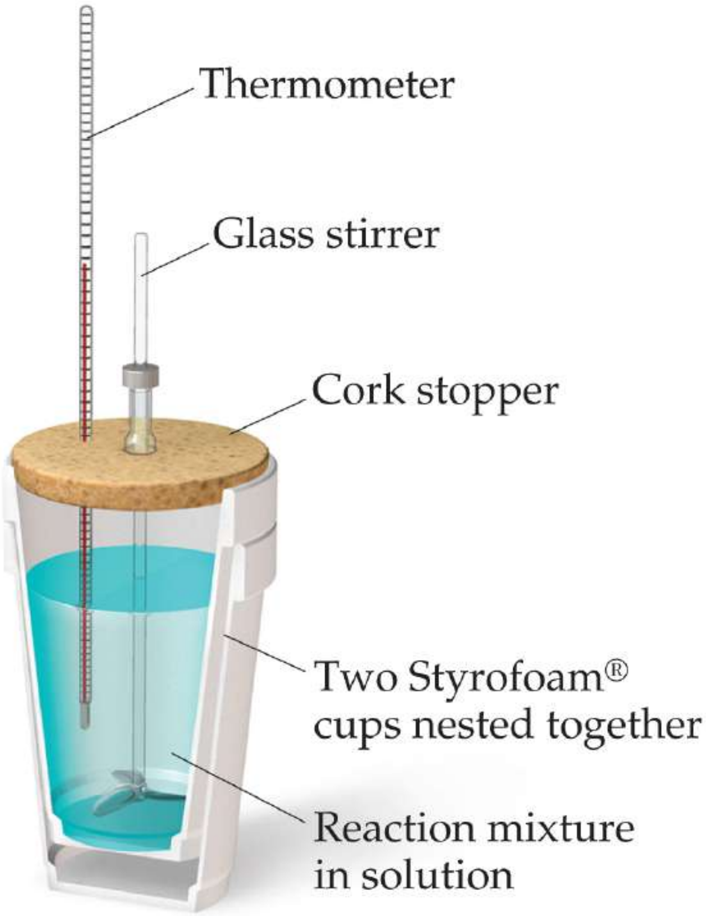
$2\ H_2O_{2(l)} \longrightarrow 2\ H_2O_{(l)} + O_{2(g)}$

$\Delta H = -196\ \text{kJ}$

Calculate the value of *q* when 5.00 g of $H_2O_{2(l)}$ decomposes at constant pressure.

5.5 CALORIMETRY

CALORIMETRY



Since we cannot know the exact enthalpy of the reactants and products, we measure ΔH through **calorimetry**, the measurement of heat flow.

The instrument used to measure heat flow is called a **calorimeter.**

HEAT CAPACITY AND SPECIFIC HEAT

The amount of energy required to raise the temperature of a substance by 1 K (1 °C) is its **heat capacity**, usually given for one mole of the substance

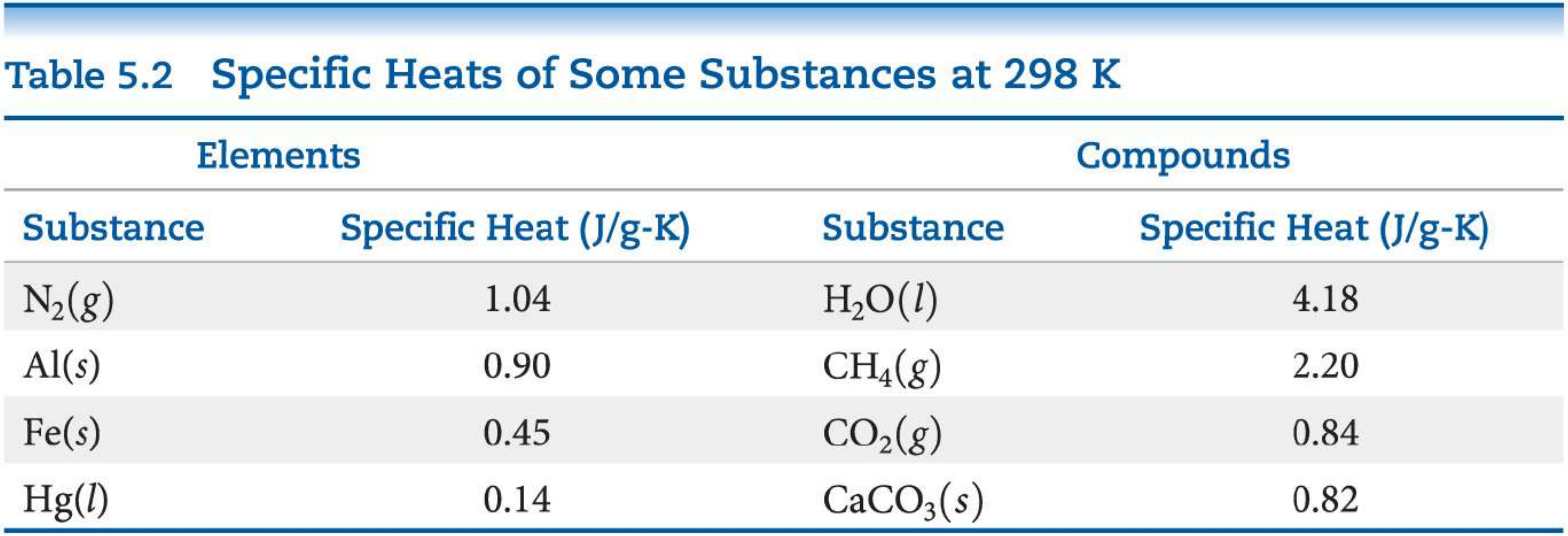


Table 5.2 Specific Heats of Some Substances at 298 K

Elements		Compounds	
Substance	**Specific Heat (J/g-K)**	**Substance**	**Specific Heat (J/g-K)**
$N_2(g)$	1.04	$H_2O(l)$	4.18
$Al(s)$	0.90	$CH_4(g)$	2.20
$Fe(s)$	0.45	$CO_2(g)$	0.84
$Hg(l)$	0.14	$CaCO_3(s)$	0.82

Which substance in Table 5.2 undergoes the greatest temperature change when the same mass of each substance absorbs the same quantity of heat?

a. Hg(*l*)c.Al(*s*)

b. Fe(*s*)d.H_2O(*l*)

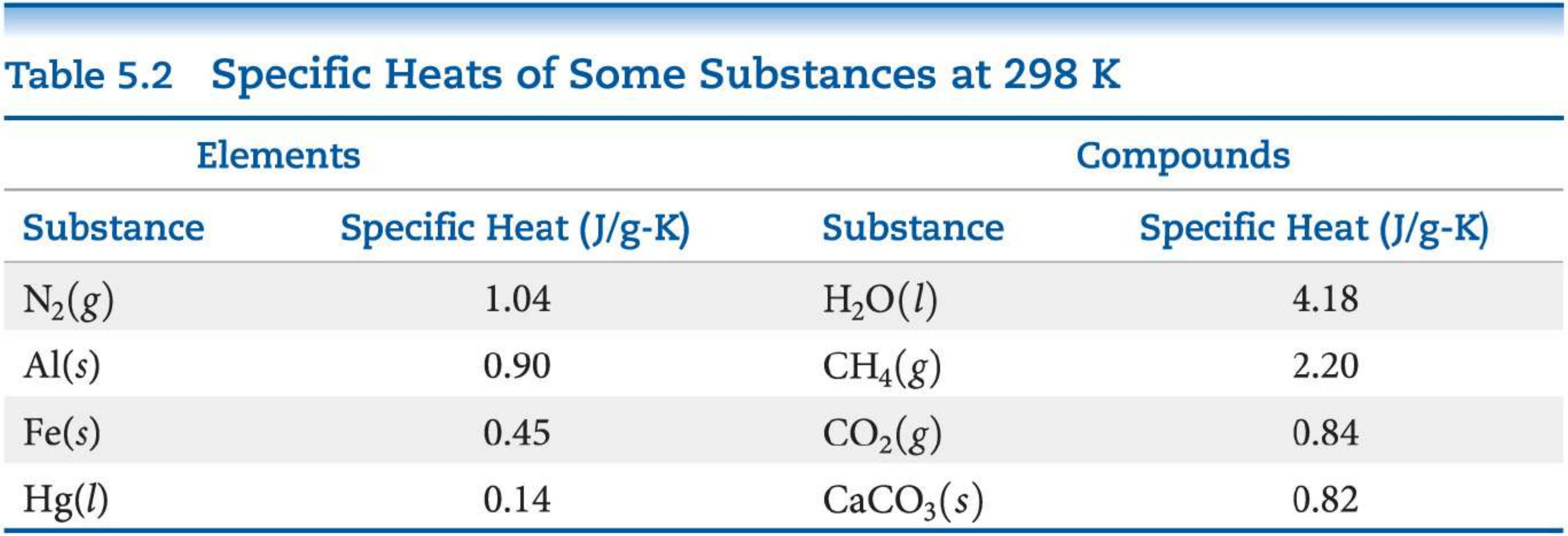
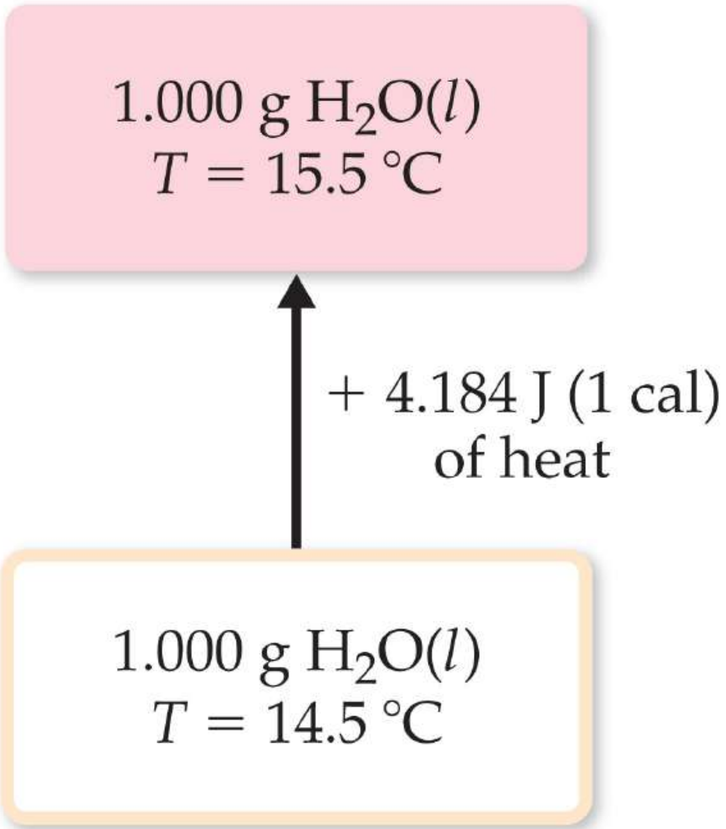


Table 5.2 Specific Heats of Some Substances at 298 K

Elements		Compounds	
Substance	**Specific Heat (J/g-K)**	**Substance**	**Specific Heat (J/g-K)**
$N_2(g)$	1.04	$H_2O(l)$	4.18
$Al(s)$	0.90	$CH_4(g)$	2.20
$Fe(s)$	0.45	$CO_2(g)$	0.84
$Hg(l)$	0.14	$CaCO_3(s)$	0.82

HEAT CAPACITY AND SPECIFIC HEAT

We define **specific heat capacity** (or simply **specific heat**) as the amount of energy required to raise the temperature of 1 g of a substance by 1 K (or 1 °C).



1.000 g $H_2O(l)$
$T = 15.5\ °C$

+ 4.184 J (1 cal) of heat

1.000 g $H_2O(l)$
$T = 14.5\ °C$

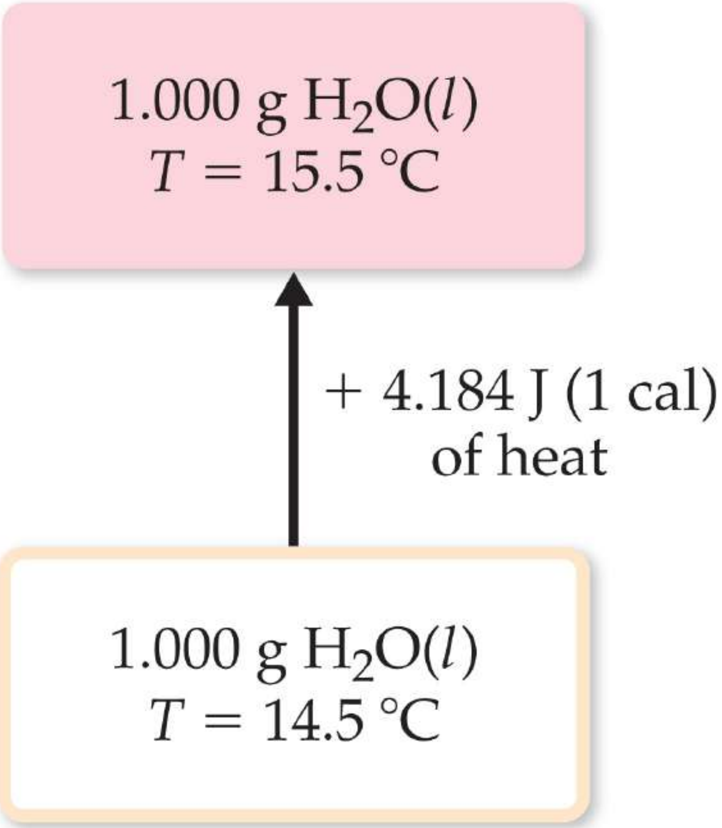
Is the process shown in the figure endothermic or exothermic?

a. Exothermic, because the temperature of the system increases

b. Exothermic, because the temperature of the system decreases

c. Endothermic, because the temperature of the system increases

d. Endothermic, because the temperature of the system decreases



HEAT CAPACITY AND SPECIFIC HEAT

Specific heat, then, is

$$\text{Specific heat} = \frac{\text{heat transferred}}{\text{mass} \times \text{temperature change}}$$

$$C_s = \frac{q}{m \times \Delta T}$$

SAMPLE EXERCISE 5.6

(**a**) How much heat is needed to warm 250 g of water (about 1 cup) from 22 °C (about room temperature) to near its boiling point, 98 °C? The specific heat of water is 4.18 J/g-K. (**b**) What is the molar heat capacity of water?

Practice Exercise 1

Suppose you have equal masses of two substances, A and B. When the same amount of heat is added to samples of each, the temperature of A increases by 14 °C whereas that of B increases by 22 °C. Which of the following statements is true?

(a) The heat capacity of B is greater than that of A.
(b) The specific heat of A is greater than that of B.
(c) The molar heat capacity of B is greater than that of A.
(d) The volume of A is greater than that of B.
(e) The molar mass of A is greater than that of B.

PRACTICE EXERCISE 2

A) Large beds of rocks are used in some solar-heated homes to store heat. Assume the specific heat of the rock is 0.82 J/g-K. Calculate the quantity of heat absorbed by 50.0 kg of rocks if their temperature increases by 12.0°C.

B) What temperature change would these rocks undergo if they emitted 450 kJ of heat?

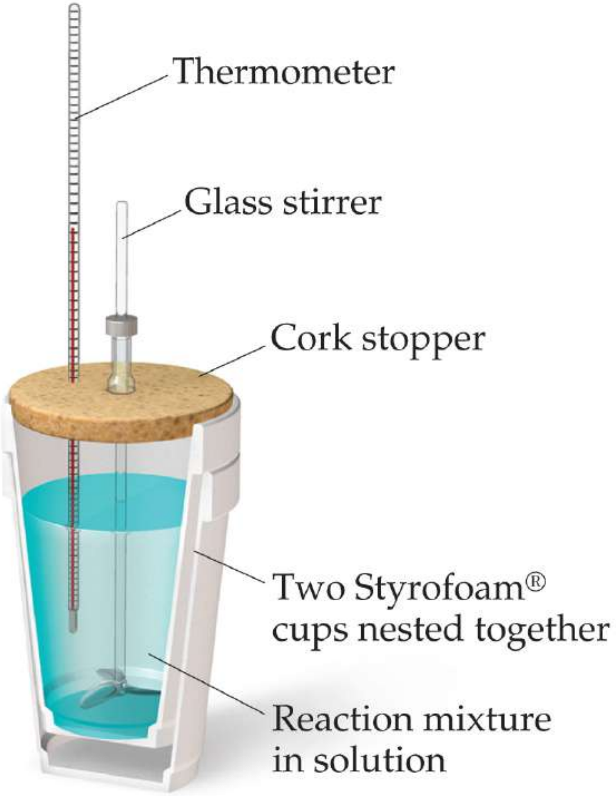
CONSTANT PRESSURE CALORIMETRY

By carrying out a reaction in aqueous solution in a simple calorimeter, the heat change for the system can be found by measuring the heat change for the water in the calorimeter.

The specific heat for water is well known (4.184 J/g·K).

We can calculate Δ*H* for the reaction with this equation:

$$q = m \times C_s \times \Delta T$$



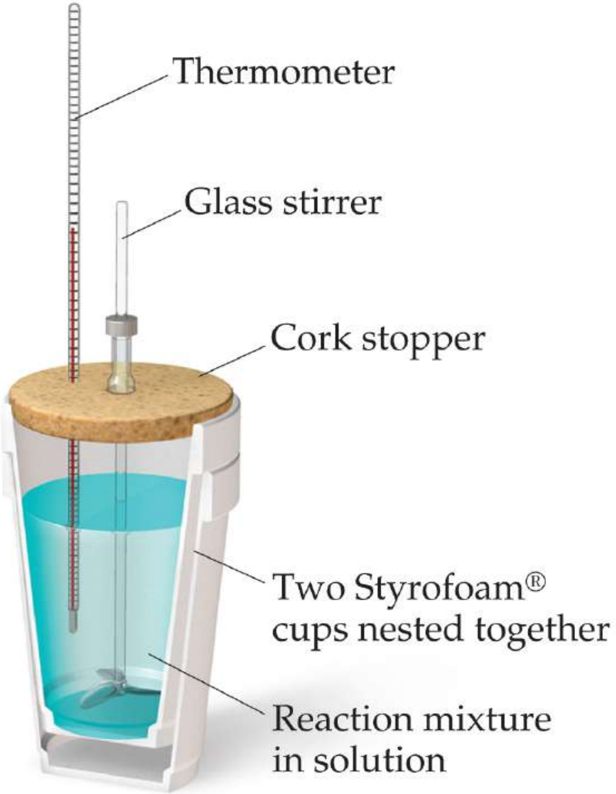
Propose a reason for why two Styrofoam® cups are often used instead of just one.

a. Styrofoam cups are very fragile

b. To create a vacuum between the two cups

c. To give greater support to the equipment setup

d. To provide more thermal insulation



SAMPLE EXERCISE 5.7

When a student mixes 50 mL of 1.0 *M* HCl and 50 mL of 1.0 *M* NaOH in a coffee-cup calorimeter, the temperature of the resultant solution increases from 21.0 °C to 27.5 °C. Calculate the enthalpy change for the reaction in kJ/mol HCl, assuming that the calorimeter loses only a negligible quantity of heat, that the total volume of the solution is 100 mL, that its density is 1.0 g/mL, and that its specific heat is 4.18 J/g-K.

Practice Exercise 1

When 0.243 g of Mg metal is combined with enough HCl to make 100 mL of solution in a constant-pressure calorimeter, the following reaction occurs:

$$Mg(s) + 2\ HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$$

If the temperature of the solution increases from 23.0 to 34.1 ° C as a result of this reaction, calculate ΔH in kJ/mol Mg. Assume that the solution has a specific heat of 4.18 J/g- °C.

(a) −19.1 kJ/mol

(b) −111 kJ/mol

(c) −191 kJ/mol

(d) −464 kJ/mol

(e) −961 kJ/mol

PRACTICE EXERCISE 2

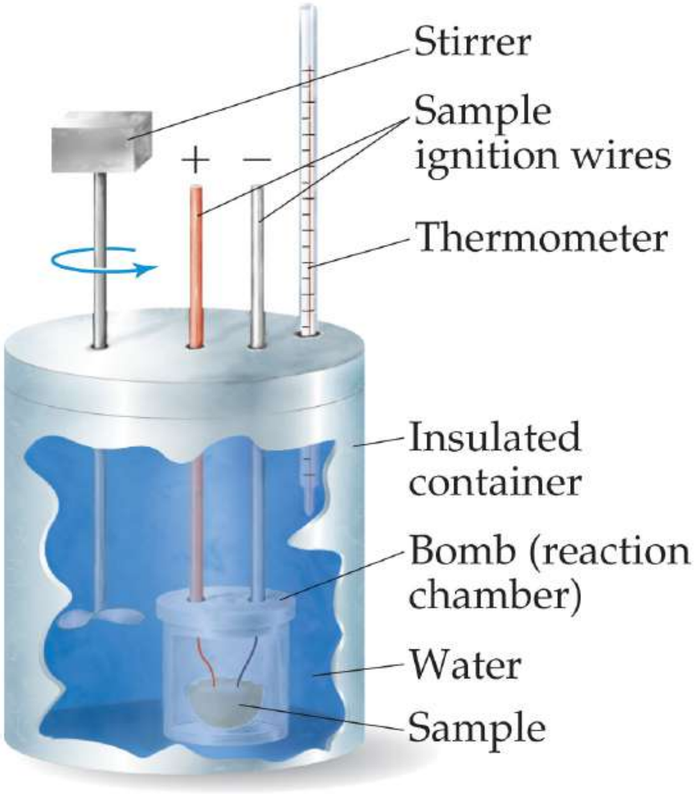
When 50.0 mL of 0.100 M $AgNO_3$ and 50.0 mL of 0.100 M HCl are mixed in a constant-pressure calorimeter, the temperature of the mixture increases from 22.30°C to 23.11°C due to the reaction. Calculate ΔH for this reaction in kJ/mol $AgNO_3$, assuming that the combined solution has a mass of 100.0 g and a specific heat of 4.18 J/g°C

BOMB CALORIMETRY

Reactions can be carried out in a sealed "bomb" such as this one.

The heat absorbed (or released) by the water is a very good approximation of the enthalpy change for the reaction.

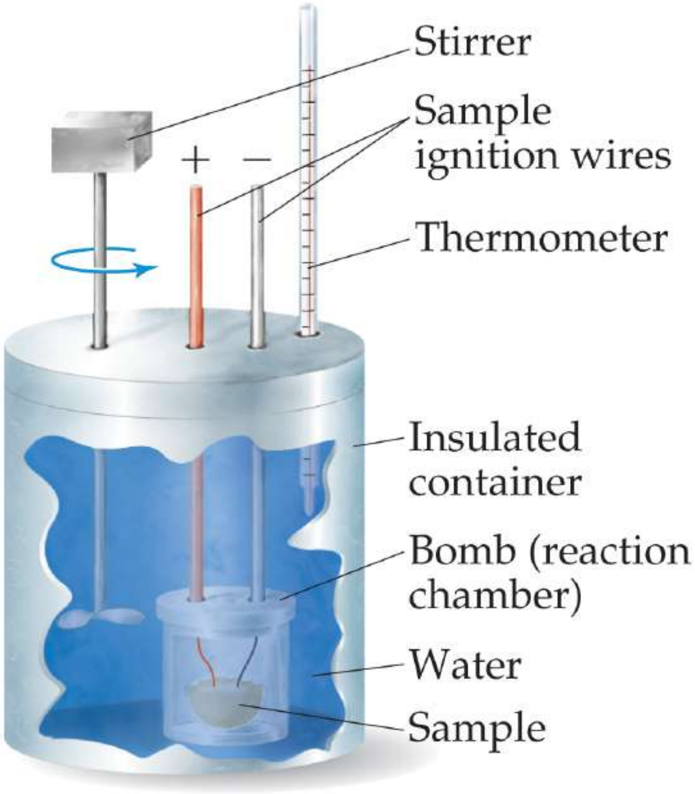
$q_{rxn} = -C_{cal} \times \Delta T$



BOMB CALORIMETRY

Because the volume in the bomb calorimeter is constant, what is measured is really the change in internal energy, ΔE, not ΔH.

For most reactions, the difference is very small.



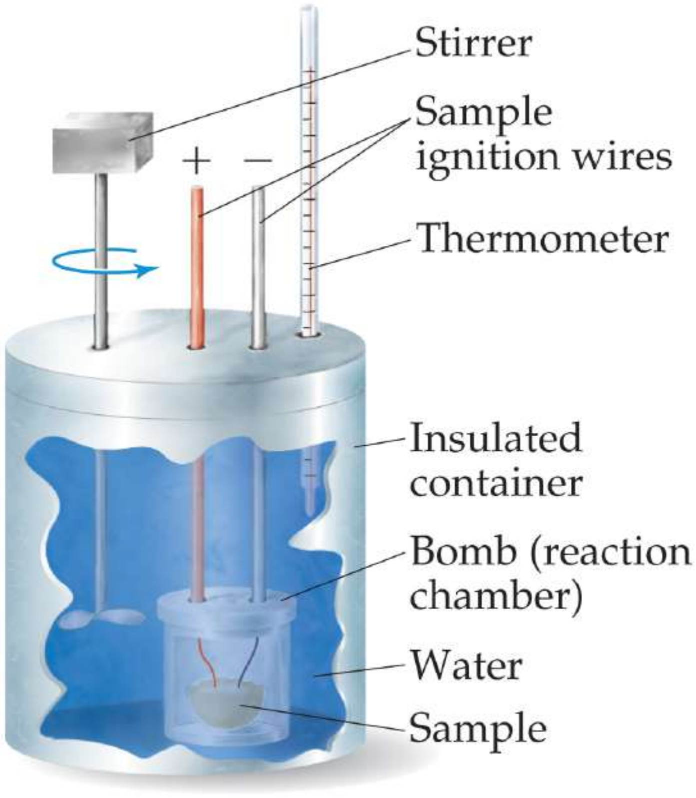
Why is a stirrer used in calorimeters?

a. Ensures a heterogeneous mixture

b. Keeps particles slowly moving

c. Ensures solution is at same temperature

d. Permits titration of the solution



SAMPLE EXERCISE 5.8

Methylhydrazine (CH_6N_2) is used as a liquid rocket fuel. The combustion of methylhydrazine with oxygen produces $N_{2(g)}$, $CO_{2(g)}$, and $H_2O_{(l)}$:

$$2CH_6N_{2(l)} + 5O_{2(g)} \rightarrow 2N_{2(g)} + 2CO_{2(g)} + 6H_2O_{(l)}$$

When 4.00 g of methylhydrazine is combusted in a bomb calorimeter, the temperature of the calorimeter increases from 25.00 °C to 39.50 °C. In a separate experiment the heat capacity of the calorimeter is measured to be 7.794 kJ/°C. Calculate the heat of reaction for the combustion of a mole of CH_6N_2.

Practice Exercise 1

The combustion of exactly 1.000 g of benzoic acid in a bomb calorimeter releases 26.38 kJ of heat. If the combustion of 0.550 g of benzoic acid causes the temperature of the calorimeter to increase from 22.01 to 24.27 °C, calculate the heat capacity of the calorimeter.

(a) 0.660 kJ/°C

(b) 6.42 kJ/°C

(c) 14.5 kJ/°C

(d) 21.2 kJ/g- °C

(e) 32.7 kJ/°C

PRACTICE EXERCISE 2

A 0.5865-g sample of lactic acid ($HC_3H_5O_3$) is burned in a calorimeter whose heat capacity is 4.182 kJ/°C. The temperature increases from 23.10°C to 24.95°C. Calculate the heat of combustion of lactic acid **per gram** and **per mole.**

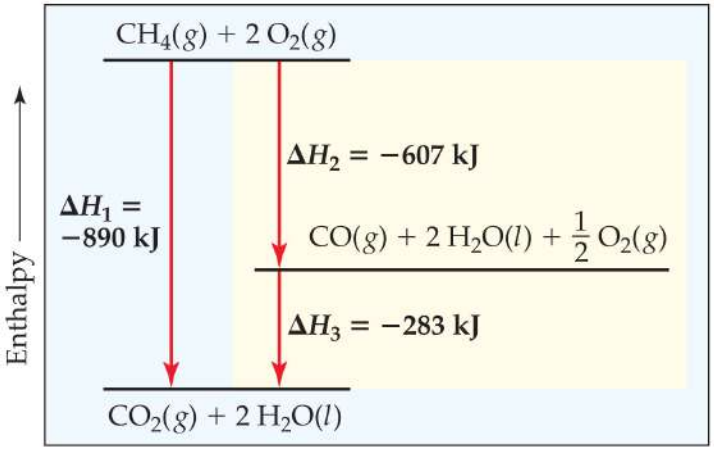
5.6 HESS’S LAW

HESS'S LAW

- ΔH is well known for many reactions, and it is inconvenient to measure ΔH for every reaction in which we are interested.

  However, we can estimate ΔH using published ΔH values and the properties of enthalpy.

HESS'S LAW



Hess's law: If a reaction is carried out in a series of steps, ΔH for the overall reaction will be equal to the sum of the enthalpy changes for the individual steps.

Because ΔH is a state function, the total enthalpy change depends only on the initial state (reactants) and the final state (products) of the reaction.

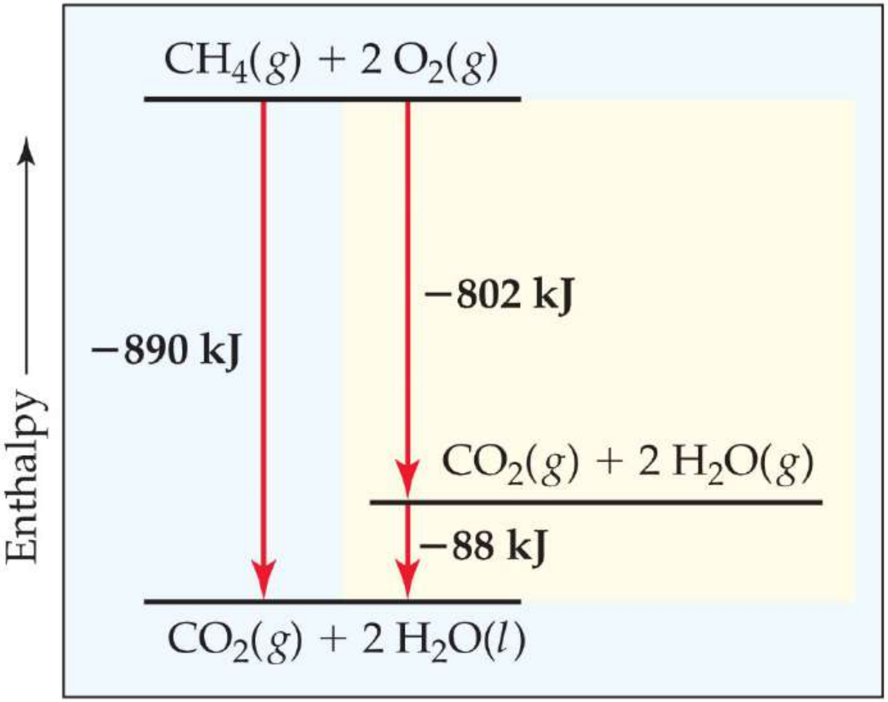
What process corresponds to the –88 kJ enthalpy change?

a. Condensation of 2 $H_2O(g)$ to 2 $H_2O(l)$

b. Vaporization of 2 $H_2O(l)$ to 2 $H_2O(g)$

c. Conversion of 2 $H_2O(l)$ to 2 $O_2(g)$

d. Conversion of $CO_2(g)$ to $CH_4(g)$



What effect do these changes have on Δ*H* for a reaction:

Reversing the reaction

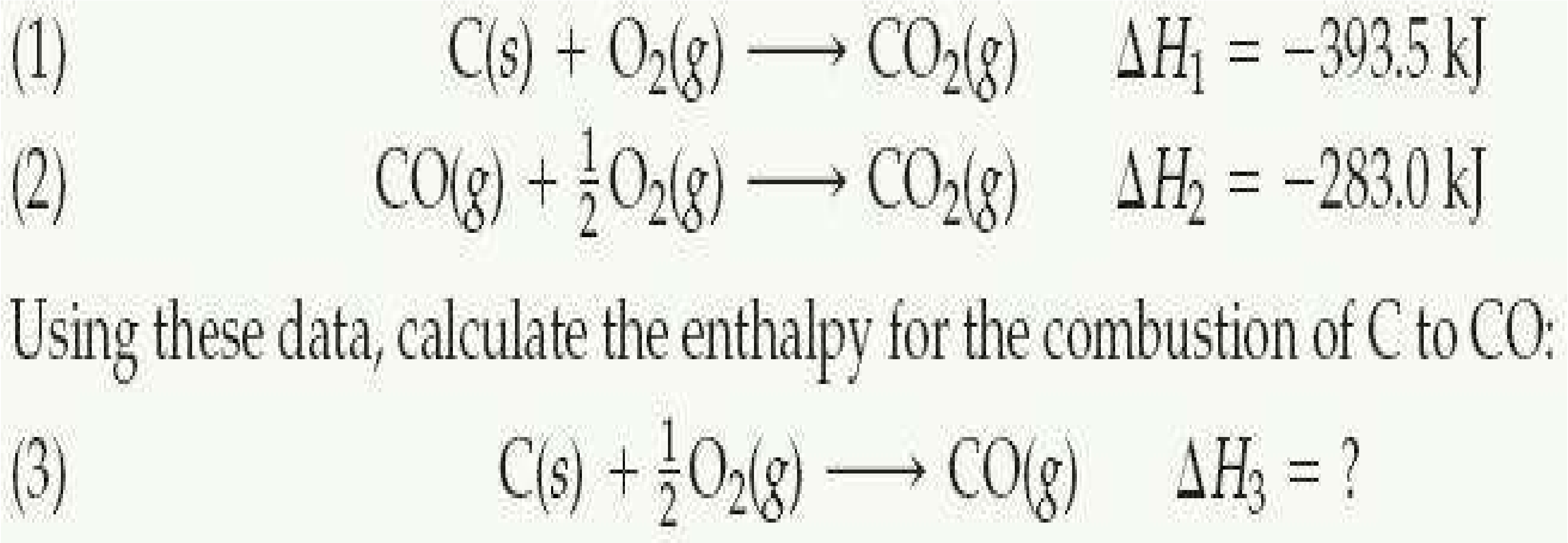
a. There is no change.
b. The sign of Δ*H* changes.
c. The value of Δ*H* increases.
d. The value of Δ*H* decreases.

What effect do these changes have on ΔH for a reaction:

Multiplying the coefficients of the equation for the reaction by 2?

a. There is no change.
b. The sign of ΔH changes.
c. The value of ΔH doubles.
d. The value of ΔH decreases by half.

SAMPLE EXERCISE 5.9



(1) $C(s) + O_2(g) \longrightarrow CO_2(g) \quad \Delta H_1 = -393.5\ \text{kJ}$

(2) $CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g) \quad \Delta H_2 = -283.0\ \text{kJ}$

Using these data, calculate the enthalpy for the combustion of C to CO:

(3) $C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g) \quad \Delta H_3 = ?$

Practice Exercise 1

Calculate ΔH for $2NO(g) + O_2(g) \rightarrow N_2O_4(g)$, using the following information:

$N_2O_4(g) \rightarrow 2NO_2(g)$ $\quad \Delta H = +57.9$ kJ

$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ $\quad \Delta H = -113.1$ kJ

(a) 2.7 kJ

(b) −55.2 kJ

(c) −85.5 kJ

(d) −171.0 kJ

(e) +55.2 kJ

PRACTICE EXERCISE 2

Carbon occurs in two forms, graphite and diamond. The enthalpy of the combustion of graphite is –393.5 kJ/mol and that of diamond is –395.4 kJ/mol:

$$\begin{aligned} \mathrm{C}(\textit{graphite}) + \mathrm{O_2}(g) &\longrightarrow \mathrm{CO_2}(g) \qquad \Delta H_1 = -393.5\ \mathrm{kJ} \\ \mathrm{C}(\textit{diamond}) + \mathrm{O_2}(g) &\longrightarrow \mathrm{CO_2}(g) \qquad \Delta H_2 = -395.4\ \mathrm{kJ} \end{aligned}$$

Calculate for the conversion of graphite to diamond:

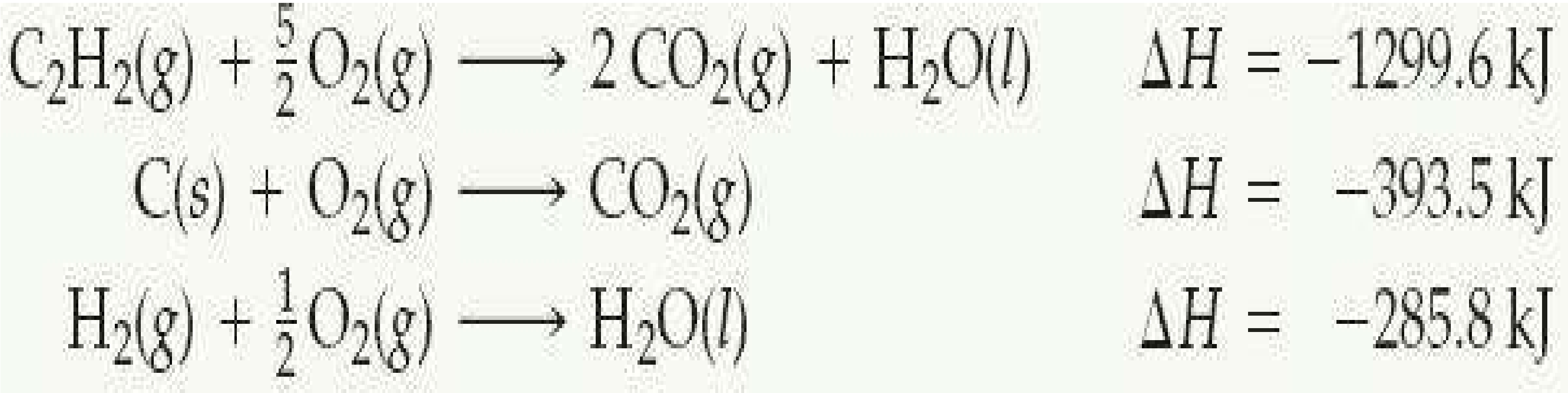
$$\mathrm{C}(\textit{graphite}) \longrightarrow \mathrm{C}(\textit{diamond}) \qquad \Delta H_3 = ?$$

SAMPLE EXERCISE 5.10

Calculate Δ*H* for the reaction

$2\ C_{(s)} + H_{2(g)} \longrightarrow C_2H_{2(g)}$

given the following chemical equations and their respective enthalpy changes



$$C_2H_2(g) + \tfrac{5}{2}O_2(g) \longrightarrow 2\,CO_2(g) + H_2O(l) \qquad \Delta H = -1299.6\text{ kJ}$$

$$C(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H = -393.5\text{ kJ}$$

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta H = -285.8\text{ kJ}$$

Practice Exercise 1

We can calculate ΔH for the reaction

$$C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$$

using the following thermochemical equations:

$C(s) + O_2(g) \rightarrow CO_2(g)\ \ \Delta H_1 = -393.5\text{ kJ}$

$2\ CO(g) + O_2(g) \rightarrow 2\ CO_2(g)\ \ \Delta H_2 = -566.0\text{ kJ}$

$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(g)\ \ \Delta H_3 = -483.6\text{ kJ}$

By what coefficient do you need to multiply ΔH_2 in determining ΔH for the target equation?

(a) –1 / 2

(b) –1

(c) 2

(d) 1 / 2

(e) 2

PRACTICE EXERCISE 2

Calculate ΔH for the reaction

$NO_{(g)} + O_{(g)} \rightarrow NO_{2(g)}$

Given the following information:

$NO_{(g)} + O_{3(g)} \rightarrow NO_{2(g)} + O_{2(g)} \quad \Delta H = -198.9\ kJ$

$O_{3(g)} \rightarrow 3/2O_{2(g)} \Delta H = -142.3\ kJ$

$O_{2(g)} \rightarrow 2O_{(g)} \qquad \Delta H = 495.0\ kJ$

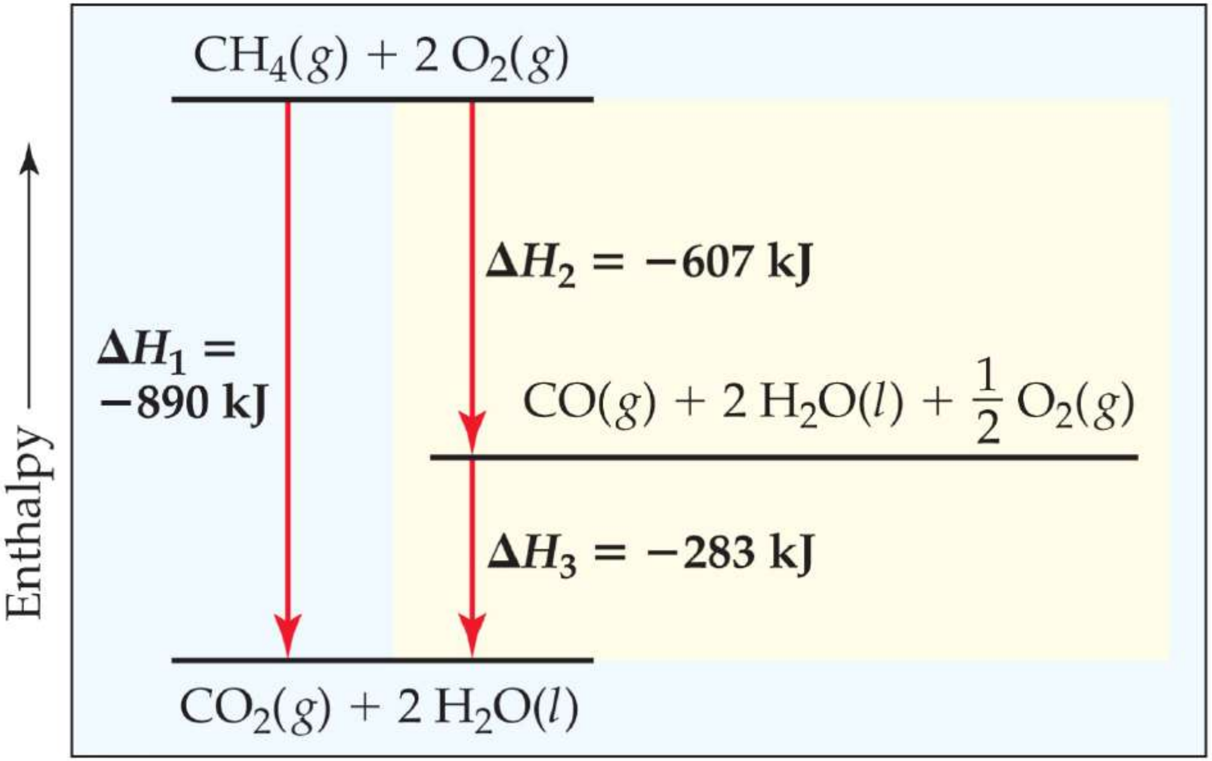
Suppose the overall reaction were modified to produce 2 $H_2O(g)$ rather than 2 $H_2O(l)$. Would any of the values of ΔH in the diagram stay the same?

a. All would change.

b. None would change.

c. ΔH_3 does not change.

d. ΔH_1 does not change.



5.7 ENTHALPIES OF FORMATION

ENTHALPIES OF FORMATION

An **enthalpy of formation,** ΔH_f, is defined as the enthalpy change for the reaction in which a compound is made from its constituent elements in their elemental forms.

STANDARD ENTHALPIES OF FORMATION

Standard enthalpies of formation, $\Delta H_f°$, are measured under standard conditions (25 °C and 1.00 atm pressure).

For elements in their most stable state at standard conditions, $\Delta H_f° = 0$

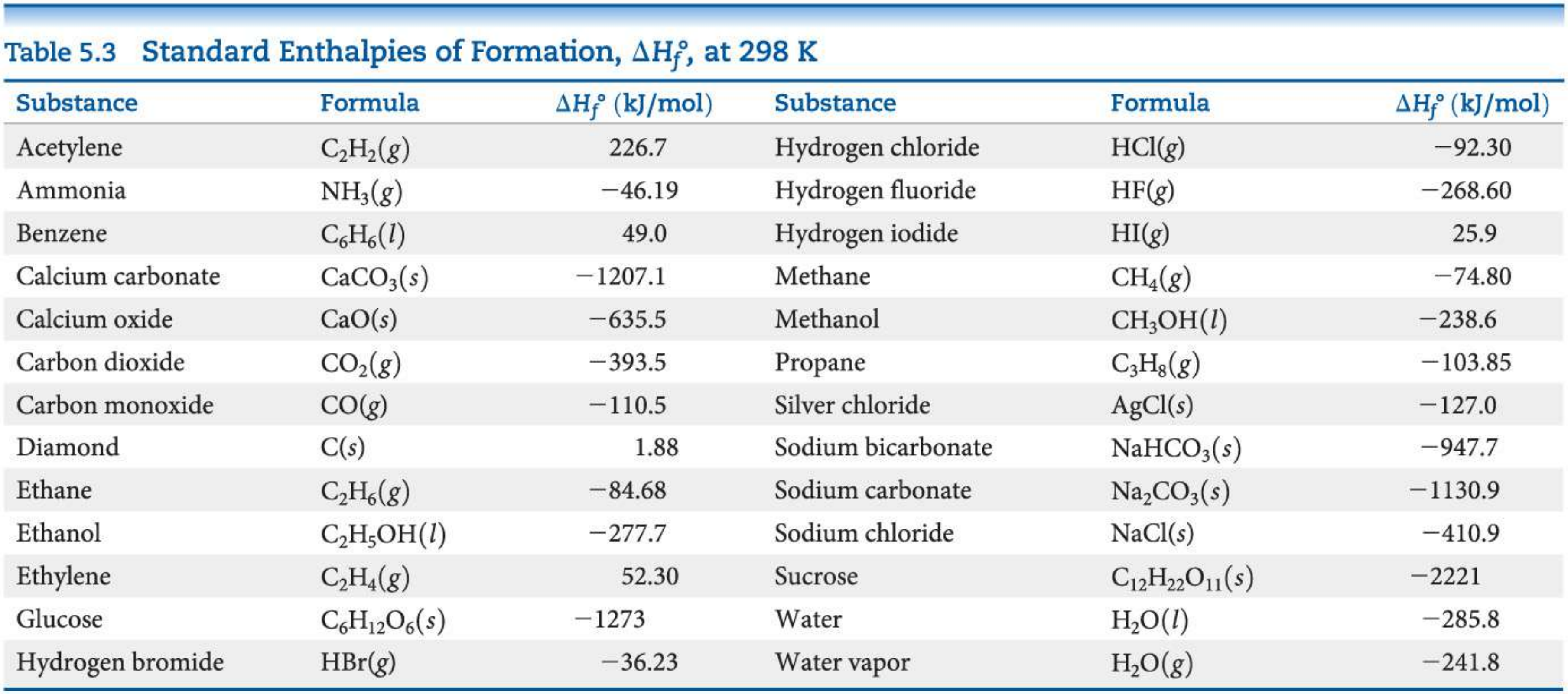


Table 5.3 Standard Enthalpies of Formation, ΔH_f°, at 298 K

Substance	Formula	ΔH_f° (kJ/mol)	Substance	Formula	ΔH_f° (kJ/mol)
Acetylene	$C_2H_2(g)$	226.7	Hydrogen chloride	$HCl(g)$	−92.30
Ammonia	$NH_3(g)$	−46.19	Hydrogen fluoride	$HF(g)$	−268.60
Benzene	$C_6H_6(l)$	49.0	Hydrogen iodide	$HI(g)$	25.9
Calcium carbonate	$CaCO_3(s)$	−1207.1	Methane	$CH_4(g)$	−74.80
Calcium oxide	$CaO(s)$	−635.5	Methanol	$CH_3OH(l)$	−238.6
Carbon dioxide	$CO_2(g)$	−393.5	Propane	$C_3H_8(g)$	−103.85
Carbon monoxide	$CO(g)$	−110.5	Silver chloride	$AgCl(s)$	−127.0
Diamond	$C(s)$	1.88	Sodium bicarbonate	$NaHCO_3(s)$	−947.7
Ethane	$C_2H_6(g)$	−84.68	Sodium carbonate	$Na_2CO_3(s)$	−1130.9
Ethanol	$C_2H_5OH(l)$	−277.7	Sodium chloride	$NaCl(s)$	−410.9
Ethylene	$C_2H_4(g)$	52.30	Sucrose	$C_{12}H_{22}O_{11}(s)$	−2221
Glucose	$C_6H_{12}O_6(s)$	−1273	Water	$H_2O(l)$	−285.8
Hydrogen bromide	$HBr(g)$	−36.23	Water vapor	$H_2O(g)$	−241.8

Ozone, $O_3(g)$, is a form of elemental oxygen produced during electrical discharge. Is ΔH°_f for $O_3(g)$ necessarily zero?

a. Yes, because it is just another elemental form of oxygen.

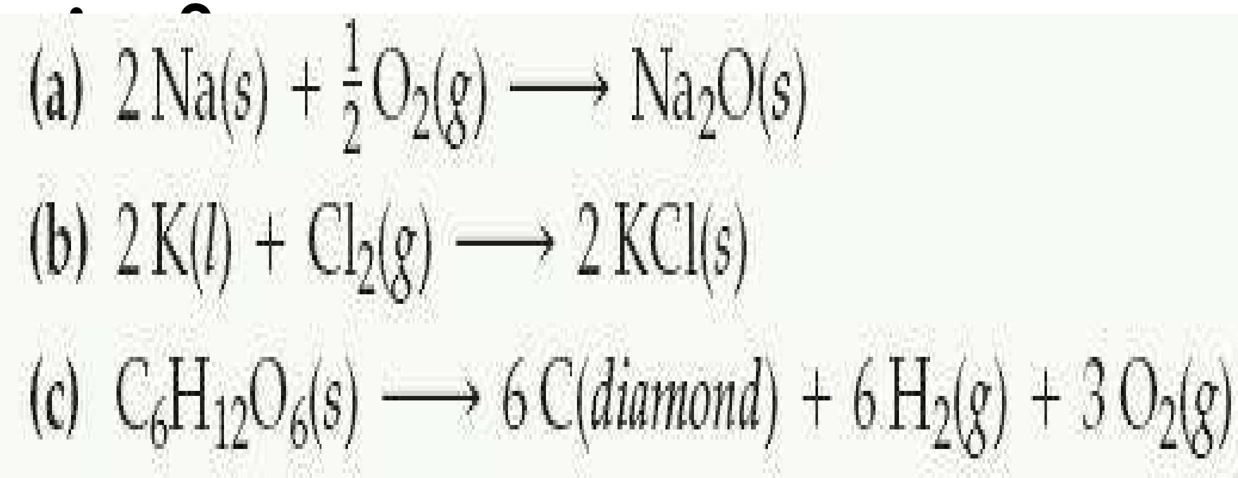
b. No, because it is not the most stable form of the element oxygen at the given conditions.

c. Yes, because changing the subscripts of an elemental formula does not change the standard heat of formation.

d. No, because there is a temperature change when ozone is formed.

SAMPLE EXERCISE 5.11

For which of the following reactions at 25°C would the enthalpy change represent a standard enthalpy of formation? For each that does not, what changes are needed to make it an equation whose ΔH is an enthalpy of form



(a) $2\,Na(s) + \frac{1}{2}O_2(g) \longrightarrow Na_2O(s)$

(b) $2\,K(l) + Cl_2(g) \longrightarrow 2\,KCl(s)$

(c) $C_6H_{12}O_6(s) \longrightarrow 6\,C(diamond) + 6\,H_2(g) + 3\,O_2(g)$

Practice Exercise 1

If the heat of formation of $H_2O(l)$ is $-286\ \text{kJ/mol}$, which of the following thermochemical equations is correct?

(a) $2H(g) + O(g) \longrightarrow H_2O(l)\ \Delta H = -286\ \text{kJ}$

(b) $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)\ \Delta H = -286\ \text{kJ}$

(c) $H_2(g) + \quad O_2(g) \longrightarrow H_2O(l)\ \Delta H = -286\ \text{kJ}$

(d) $H_2(g) + O(g) \longrightarrow H_2O(g)\ \Delta H = -286\ \text{kJ}$

(e) $H_2O(l) \longrightarrow H_2(g) + \quad O_2(g)\ \Delta H = -286\ \text{kJ}$

PRACTICE EXERCISE 2

Write the equation corresponding to the standard enthalpy of formation of liquid carbon tetrachloride (CCl_4) and look up $\Delta H_f°$ for this compound in Appendix C.

CALCULATION OF ΔH

$$C_3H_8(g) + 5\ O_2(g) \longrightarrow 3\ CO_2(g) + 4\ H_2O(l)$$

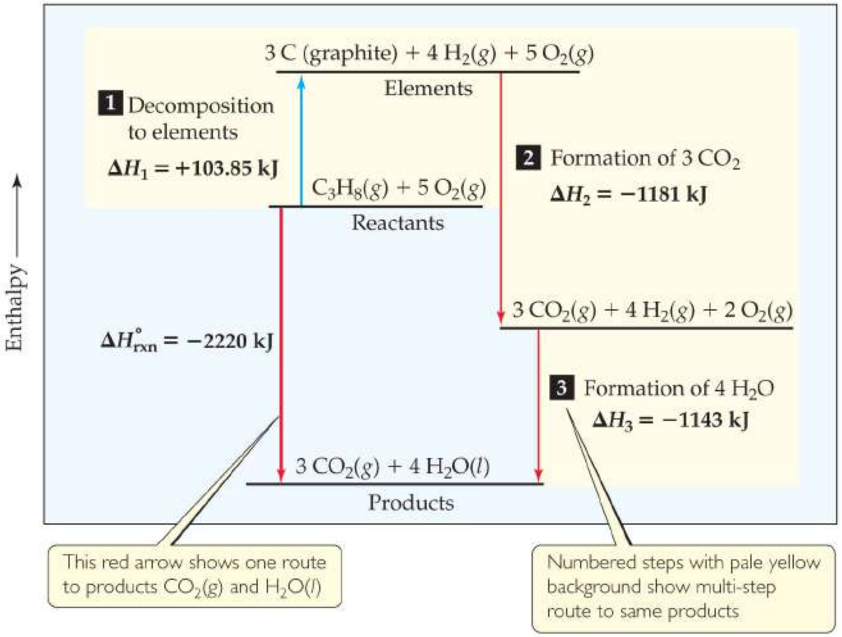
The sum of these equations is the overall equation!

$$C_3H_8(g) \longrightarrow 3\ C_{(graphite)} + 4\ H_2(g)$$

$$3\ C_{(graphite)} + 3\ O_2(g) \longrightarrow 3\ CO_2(g)$$

$$4\ H_2(g) + 2\ O_2(g) \longrightarrow 4\ H_2O(l)$$

$$C_3H_8(g) + 5\ O_2(g) \longrightarrow 3\ CO_2(g) + 4\ H_2O(l)$$



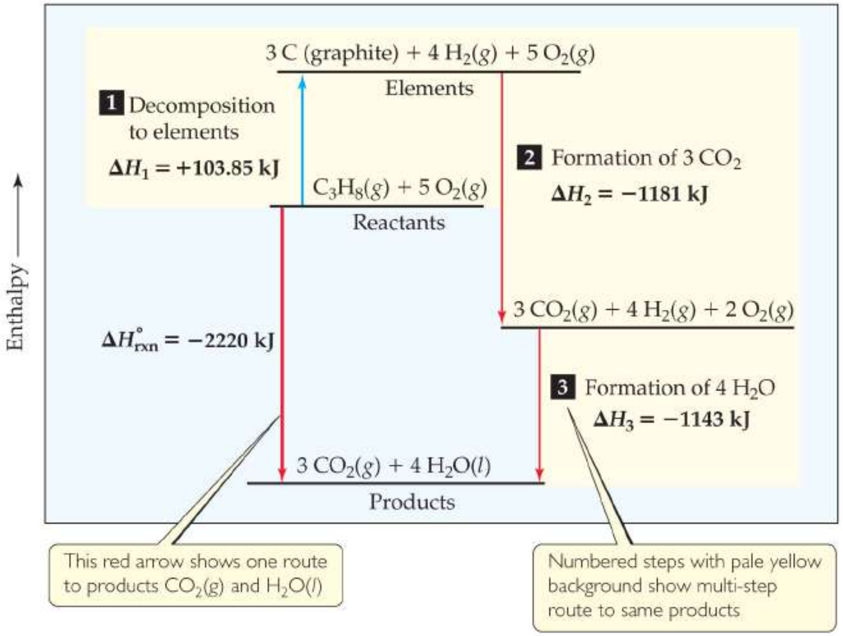
CALCULATION OF ΔH USING VALUES FROM THE STANDARD ENTHALPY TABLE

$$C_3H_8(g) + 5\ O_2(g) \longrightarrow 3\ CO_2(g) + 4\ H_2O(l)$$

$$\Delta H = [3(-393.5\text{ kJ}) + 4(-285.8\text{ kJ})] - [1(-103.85\text{ kJ}) + 5(0\text{ kJ})]$$

$$= [(-1180.5\text{ kJ}) + (-1143.2\text{ kJ})] - [(-103.85\text{ kJ}) + (0\text{ kJ})]$$

$$= (-2323.7\text{ kJ}) - (-103.85\text{ kJ}) \quad = \quad -2219.9\text{ kJ}$$



This red arrow shows one route to products $CO_2(g)$ and $H_2O(l)$

Numbered steps with pale yellow background show multi-step route to same products

CALCULATION OF ΔH

We can use Hess's law in this way:

$$\Delta H = \sum n\Delta H_{f,\text{products}} - \sum m\Delta H_f{}^\circ{}_{,\text{reactants}}$$

where *n* and *m* are the stoichiometric coefficients.

SAMPLE EXERCISE 5.12

Calculate the standard enthalpy change for the combustion of 1 mol of benzene $C_6H_6(l)$, to form $CO_2(g)$ and $H_2O(l)$. Compare the quantity of heat produced by 1.00 g propane to that produced by 1.00 g benzene.

Practice Exercise 1

Calculate the enthalpy change for the reaction

$2H_2O_2(l) \longrightarrow 2H_2O(l) + O_2(g)$

using enthalpies of formation:

$\Delta H_f{}^\circ(H_2O_2) = -187.8\ \mathrm{kJ/mol}\Delta H_f{}^\circ(H_2O) = -285.8\ \mathrm{kJ/mol}$

(a) −88.0 kJ

(b) −196.0 kJ

(c) +88.0 kJ

(d) +196.0 kJ

(e) more information needed

PRACTICE EXERCISE 2

Using the standard enthalpies of formation listed in Table 5.3, calculate the enthalpy change for the combustion of 1 mol of ethanol:

$$C_2H_5OH(l) + 3\,O_2(g) \longrightarrow 2\,CO_2(g) + 3\,H_2O(l)$$

SAMPLE EXERCISE 5.13

The standard enthalpy change for the reaction

$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$

Is 178.1 kJ. From the values for the standard enthalpies of formation of CaO and CO_2, calculate the standard enthalpy of formation for $CaCO_3$.

Practice Exercise 1

Given $2\ SO_2(g) + O_2(g) \rightarrow 2\ SO_3(g)$, which of the following equations is correct?

(a) $\Delta H_f°(SO_3) = \Delta H°_{rxn} - \Delta H_f°(SO_2)$

(b) $\Delta H_f°(SO_3) = \Delta H°_{rxn} + \Delta H_f°(SO_2)$

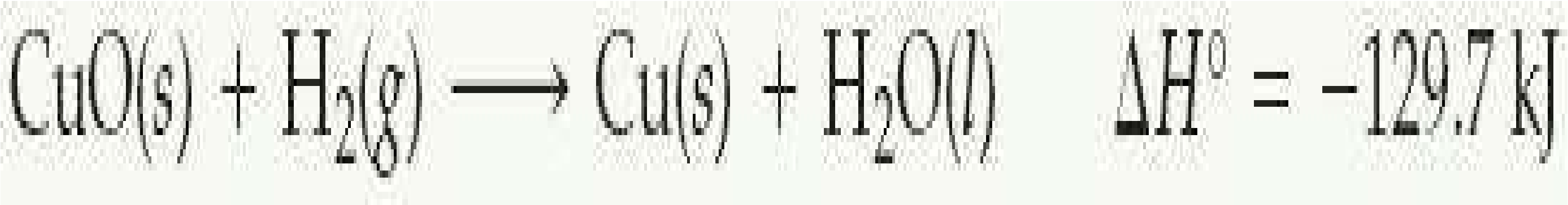
(c) $2\Delta H_f°(SO_3) = \Delta H°_{rxn} + 2\Delta H_f°(SO_2)$

(d) $2\Delta H_f°(SO_3) = \Delta H°_{rxn} - 2\Delta H_f°(SO_2)$

(e) $2\Delta H_f°(SO_3) = 2\Delta H_f°(SO_2) - \Delta H°_{rxn}$

PRACTICE EXERCISE 2

Given the following standard enthalpy change, use the standard enthalpies of formation in Table 5.3 to calculate the standard enthalpy of formation of CuO(*s*):



$$CuO(s) + H_2(g) \longrightarrow Cu(s) + H_2O(l) \qquad \Delta H^\circ = -129.7\ \mathrm{kJ}$$

5.8 FOODS AND FUELS

ENERGY IN FOODS

Most of the fuel in the food we eat comes from carbohydrates and fats.

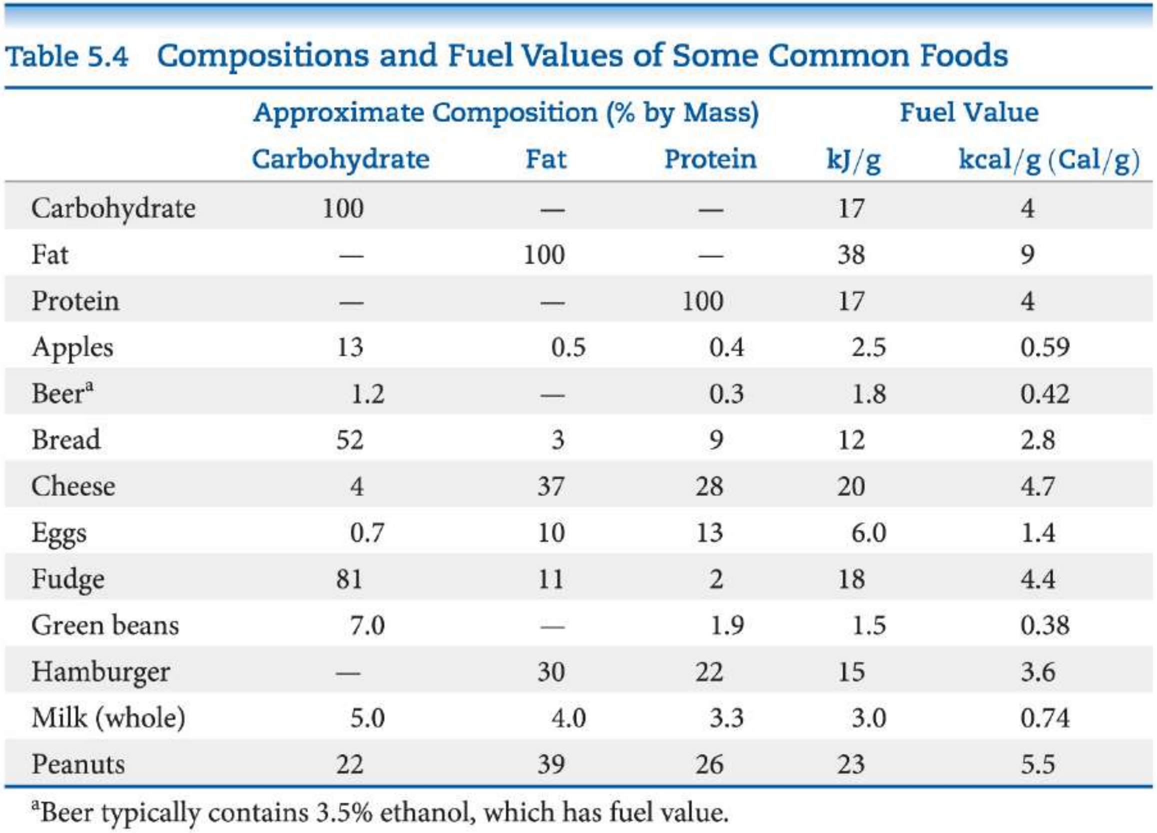


Table 5.4 Compositions and Fuel Values of Some Common Foods

	Approximate Composition (% by Mass)			Fuel Value	
	Carbohydrate	Fat	Protein	kJ/g	kcal/g (Cal/g)
Carbohydrate	100	—	—	17	4
Fat	—	100	—	38	9
Protein	—	—	100	17	4
Apples	13	0.5	0.4	2.5	0.59
Beer[a]	1.2	—	0.3	1.8	0.42
Bread	52	3	9	12	2.8
Cheese	4	37	28	20	4.7
Eggs	0.7	10	13	6.0	1.4
Fudge	81	11	2	18	4.4
Green beans	7.0	—	1.9	1.5	0.38
Hamburger	—	30	22	15	3.6
Milk (whole)	5.0	4.0	3.3	3.0	0.74
Peanuts	22	39	26	23	5.5

[a] Beer typically contains 3.5% ethanol, which has fuel value.

ENERGY IN FUELS

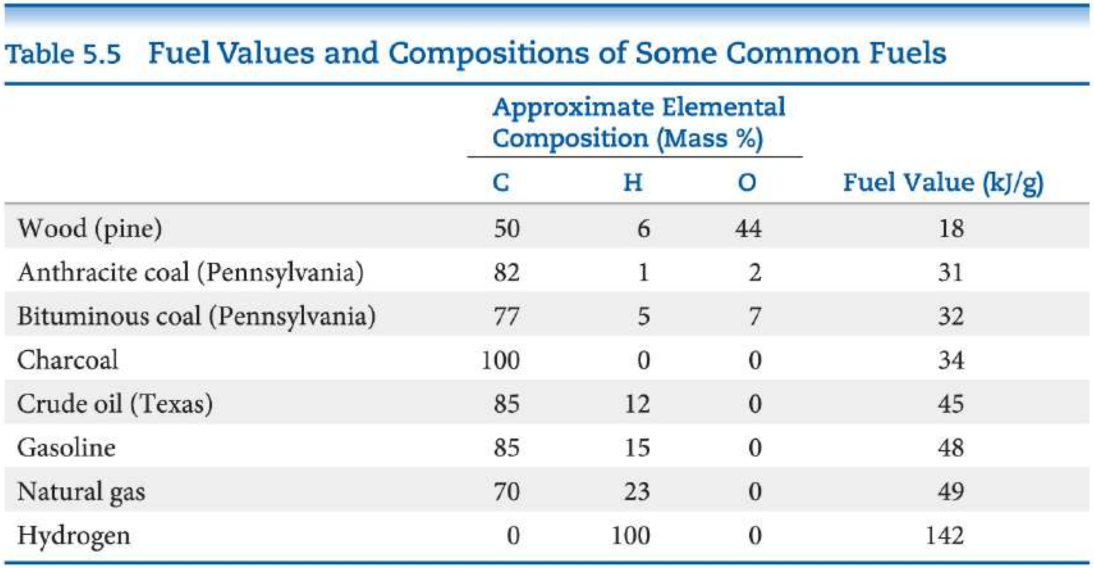
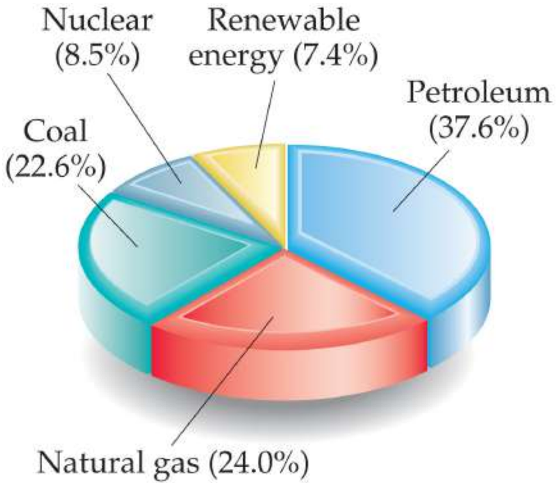


Table 5.5 Fuel Values and Compositions of Some Common Fuels

	Approximate Elemental Composition (Mass %)			
	C	**H**	**O**	**Fuel Value (kJ/g)**
Wood (pine)	50	6	44	18
Anthracite coal (Pennsylvania)	82	1	2	31
Bituminous coal (Pennsylvania)	77	5	7	32
Charcoal	100	0	0	34
Crude oil (Texas)	85	12	0	45
Gasoline	85	15	0	48
Natural gas	70	23	0	49
Hydrogen	0	100	0	142

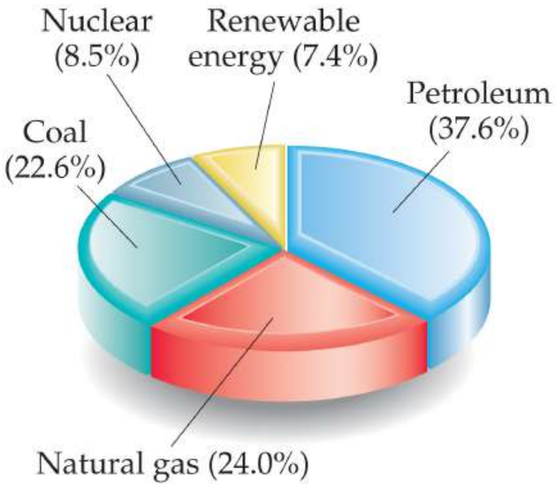


The vast majority of the energy consumed in this country comes from fossil fuels.

OTHER ENERGY SOURCES

Nuclear fission produces 8.5% of the U.S. energy needs.

Renewable energy sources, like solar, wind, geothermal, hydroelectric, and biomass sources produce 7.4% of the U.S. energy needs.



SAMPLE INTEGRATIVE EXERCISE

Trinitroglycerin, $C_3H_5N_3O_9$, decomposes to form N_2, CO_2, H_2O, and O_2 with an enthalpy of -1541.4 kJ/mol.

- A) Write the balanced chemical equation
- B) Calculate the standard heat of formation
- C) How many calories are released from a 0.60 mg dose?
- D) A common form melts at 3°C, would you expect it to be molecular or ionic?
- E) Describe the various conversions of forms of energy when trinitroglycerin is used as an explosive to break rockfaces in highway construction.